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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXVII.—1898.

45139
91/5/98

LONDON:
PUBLISHED AT THE OFFICE, 6 & 7, CREED LANE, LUDGATE HILL, E.C.
AND SOLD BY ALL BOOKSELLERS.

MDCCCXCVIII.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,
6 & 7, CREED LANE, LUDGATE HILL,
E.C.

THE CHEMICAL NEWS.

VOLUME LXXVII.

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No. 1989.—JANUARY 7, 1898.

ON THE REFRACTIVITIES OF AIR, OXYGEN, NITROGEN, ARGON, HYDROGEN, AND HELIUM.*

By Prof. WILLIAM RAMSAY, Ph.D., LL.D., Sc.D., F.R.S., and MORRIS W. TRAVERS, B.Sc.

In the course of a research on the nature of helium many measurements of its refractivity referred to that of air as unity were made by means of an apparatus similar to that described by Lord Rayleigh (*Proceedings*, vol. lix., p. 203). Inasmuch as the refractivity of helium is very small, it was not found convenient to measure its value directly against air; hence it was compared with hydrogen, and hydrogen was compared with air. And as a check on these measurements, the hydrogen was compared with oxygen, and subsequently with nitrogen free from argon. It was noticed, after some of these experiments had been made, that the refractivity of air could not be accurately calculated from the given data for oxygen, nitrogen, and argon; and it appeared therefore worth while to examine more minutely the refractivity of these gases for white light, and to see whether any error could be detected in previous measurements. Moreover, as physicists perhaps do not always devote sufficient care to the chemical purity of their materials, an additional reason was furnished for the inquiry.

Apparatus.—It will be seen, on consulting Lord Rayleigh's paper, that the refractivity is measured in the following manner:—Light from a paraffin lamp passes through a fine slit, cut with a razor in tin-foil pasted on glass. The beam is made parallel by passage through an achromatic plano-convex lens of about 1 foot focal length. It then divides; the upper portion passes through air, and, after extraneous light is cut off by passage through two wide slits, it is brought to a focus by a lens similar to the first, and the bands produced are viewed by a cylindrical lens of very short focus. The lower portion of the beam traverses two tubes, 9 inches long and ¼ of an inch in diameter, placed close together, and closed at each end with plates of optically worked glass. Each of these tubes contains one of the gases to be examined, and each is connected with a manometer and a movable reservoir; so that, on raising or lowering the reservoir, the pressure of the gases can be so adjusted that the interference-bands formed in the lower half of the field can be accurately brought into line with the stationary bands in the upper half. Readings of pressure are taken on both manometers at pressures not differing greatly from that of the atmosphere; then, on lowering the reservoirs, readings on both manometers are taken at lower pressures, the bands being again made to coincide in position with the upper fiducial bands. The ratio of the refractivities is inversely as the differences of pressure in the two gases. The influence of temperature does not appear, for the tubes of the manometer lie side by side, and may be regarded as equally affected by variations of temperature.

The accuracy of this method varies with the value of the refractivity of the gas. For if the gas has a low refractivity, then a great difference of pressure produces the passage of fewer bands across the field than if it has a high one; and, as the accuracy of reading may safely be taken as the twenty-fifth of a band; and as between thirty and forty bands passed the field with such gases as oxygen, nitrogen, and argon, the error may be taken in such cases as from 1 in 750 to 1 in 1000.

The tubes containing the gases to be examined were connected with a Töpler's pump; and before admission of gas each tube was pumped empty, so that in an attached Plücker's tube there was brilliant phosphorescence. The tubes were then washed out with the gases to be admitted, the apparatus again evacuated, and the final quantity of gas allowed to enter by a contrivance a description of which is to be found in the *Trans. Chem. Soc.*, vol. lxvii., p. 686.

Purity of the Gases. Hydrogen.—The hydrogen was made by warming a tube containing palladium hydrogen which had been prepared by admitting hydrogen made from pure zinc and sulphuric acid into contact with spongy palladium. The tube was pumped empty in the cold, and then gently warmed; it was again allowed to cool, and again pumped empty. The hydrogen was then collected passing slowly through a tube, filled with phosphoric anhydride, into the experimental tube.

Oxygen.—The oxygen was prepared by heating a small tube containing potassium permanganate; a large quantity of gas was allowed to escape, and a portion was collected finally which served for the experiments.

Nitrogen.—The nitrogen was prepared from a mixture of ammonium chloride and sodium nitrite, to which a little copper sulphate had been added. The apparatus was exhausted before admission of either of the solutions, and before allowing the solutions to enter they were boiled, and the flasks corked while boiling. The gas was

* A Paper read before the Royal Society, December 9th, 1897.

passed over red-cot copper; the ammonia liberated by the alkalinity of the nitrite thus reacted with any oxides of nitrogen possibly present to form water. The gas was collected, after rejection of a considerable portion, in a tube containing oil of vitriol; it was then transferred to a fresh tube, treated with a very strong solution of caustic potash, and finally admitted to the apparatus.

Air.—The air was left standing for some hours in a tube containing sticks of caustic potash, and was then admitted to the apparatus through a tube of phosphoric anhydride.

Experimental Data.—Each gas was compared with air and with the other two. Air is in each case taken as unity.

Hydrogen.—Hydrogen/air	0·4730	Mean	0·4733
	0·4737		
Hydrogen/oxygen ..	0·5125	,,	0·5125
	0·5125		
Hydrogen/nitrogen ..	0·4654	,,	0·4654
	0·4654		
Oxygen.—Oxygen/air	0·9237		
	0·9262	,,	0·9243
	0·9230		
Oxygen/hydrogen ..	1·9512	,,	1·9512
	1·9512		
Oxygen/nitrogen ..	0·9090		
	0·9122	,,	0·9105
	0·9103		
Nitrogen.—Nitrogen/air	1·0153		
	1·0171	,,	1·0166
	1·0174		
Nitrogen/hydrogen ..	2·1487	,,	2·1487
	2·1487		
Nitrogen/oxygen ..	1·1001		
	1·0962	,,	1·0983
	1·0986		

To these numbers those for argon must be added. The gas was prepared in the usual manner from air; and before admitting it into the experimental tube it was sparked with oxygen in presence of caustic soda for two days. The oxygen was removed with phosphorus, and the argon, on its way into the experimental tube, passed over phosphorus pentoxide; a Plücker's tube was sealed to the tube through which it entered, so that its spectrum might be observed. It contained no visible trace of either hydrogen or nitrogen.

Argon.—Argon/air	0·9596		
	0·9596	Mean	0·9596
	0·9598		
Argon/oxygen ..	1·0350		
	1·0348	,,	1·0362
	1·0381		
Argon/nitrogen ..	0·9412	,,	0·9416
	0·9419		

Placing air in each case equal to unity, and calculating the refractivities of the other gases, we obtain the following table:—

Refractivities of Gases, Air equal to Unity.

	Directly compared.	Through Oxygen.	Through Nitrogen.	Through Hydrogen.	Through Argon.
Hydrogen ..	0·4733	0·4737	0·4727	—	—
Oxygen	0·9243	—	0·9247	0·9237	0·9261
Nitrogen ..	0·0163	1·0155	—	1·0170	1·0191
Argon	0·9596	0·9577	0·9572	—	—
Carbon dioxide	—	1·5316	—	—	—

It will be seen, on inspecting the above table, that the numbers obtained indirectly are in close agreement with those obtained by direct comparison with air.

Taking the value found directly by Mascart for D,* viz., $(n-1)_D = 0{\cdot}0002923$, the values found by him for nitrogen (atmospheric) was 0·0002972, giving for nitrogen on the basis air equal to unity, the number 1·0178. Mascart did not determine the value for oxygen, but calculated it from the above data and the known composition of air. Nor did Lorenz determine the value for nitrogen, but, taking his own value for oxygen, viz., $(n-1)_D = 0{\cdot}000272$, and for air $(n-1)_D = 0{\cdot}000291$, he deduced it, as Mascart had done for oxygen. So that we have no determination of the three constants, or their comparison, by any one observer since Dulong in 1826. It has been tacitly assumed that the refractive index for a mixture of gases is that of those of their constituents, taken in the proportion in which they occur. We have in our hands a means of verifying this assumption, which is well known not to hold for compound gases, nor for mixtures of liquids, even though change of density be taken into consideration.

Dulong (*Ann. Chim. Phys.*, lxxxi., p. 176, 1826) gives very careful accounts of the methods he used in preparing the samples of gas that he employed. Oxygen, to which he ascribed the refractivity 0·924, was obtained by heating potassium chlorate. His result is identical with ours. Nitrogen was prepared from air by absorbing the oxygen with phosphorus, first at a high temperature and then in the cold. It was then washed with a solution of chlorine, and afterwards with potash. It is difficult to see what object was to be gained by washing with chlorine water, unless it was the removal of hydrogen. The number he obtained was 1·02, somewhat higher than that which we have found. Dulong also determined the refractivity of air, and, allowing for that of the small percentage of carbon dioxide, it is precisely the mean of that of its constituents, taken in the proportion in which they are present.

Returning to the results of Mascart and Lorenz, we have for the D lines:—

	Air.	Nitrogen.	Oxygen.
Mascart	1	1·0178	—
Lorenz	1	—	0·9347

From these data of Mascart and Lorenz it is possible to calculate the refractivity of air:—

$$(1{\cdot}0178 \times 79{\cdot}1) + (0{\cdot}9347 \times 20{\cdot}9) = 100{\cdot}15.$$

There is reason to doubt the purity of Lorenz's oxygen. He heated mercuric oxide, of which he does not give the method of preparation; it may have contained oxides of nitrogen; and for some reason, not explained, he passed the gas through a vacuous porcelain tube, presumably red-hot, which, as recent experiments of Messrs. Bone and Jerdan have shown (*Chem. Soc. Trans.*, 1897, p. 42), is not impervious to furnace gases. Dulong, on the other hand, who, as already remarked, prepared his oxygen from chlorate, obtained the number 0·924 for white light, coincident with our determinations.

The refractive index of air, calculated from our determinations, viz.,—

Oxygen	0·9243
Nitrogen	1·0163
Argon	0·9596

and the densities of the constituent gases ("Argon," *Phil. Trans.*, A, 1895, p. 202, footnote), gives the following numbers:—

$$(1{\cdot}0163 \times 78{\cdot}15) + (0{\cdot}9243 \times 20{\cdot}91) + (0{\cdot}9596 \times 0{\cdot}94) = 99{\cdot}653.$$

Observers sometimes find the percentage of oxygen in air to be about 20·98, or even 21·0. This would hardly affect the result; with 20·96 per cent of oxygen the calculated refractivity is 99·647, instead of 99·653.

There can be no doubt as to the refractivity of oxygen from our ratios, as well as from Dulong's determinations.

* The dispersions for these gases are so small as not to affect the ratios of these numbers (*Compt. Rend.*, 1874, lxxviii., p. 621).

The question is as regards nitrogen. It would require the refractivity of nitrogen to be 1·208, a number greatly above any of our values, in order that the sum of the refractivities of oxygen, nitrogen, and argon should equal 100. The presence of argon would also make an almost inappreciable difference. Taking Mascart's determination of the refractivity of atmospheric nitrogen to be correct, that of pure nitrogen would be 1·0181, instead of 1·0178. And an error in the refractivity of argon would also not affect the result, inasmuch as the total amount of argon is so small.

We are thus driven to conclude that the refractivity of the mixture, air, is somewhat less than that of the sum of the refractivities of its constituents, taken in the proportion in which they occur.

It appeared advisable to try other mixtures; and a mixture of hydrogen and helium was first selected, because these are both very "perfect" gases, inasmuch as their critical points lie very low. It was to be expected that if a difference between calculated and found values should exist, it should be of the inverse character to that of a mixture of oxygen and nitrogen, for they are two somewhat "imperfect" gases. The result has borne out this idea.

A mixture was made of 20·60 c.c. of hydrogen and of 20·12 c.c. of helium free from argon, and of the density 1·960; and with the refractivity of the mixture those of hydrogen and helium were compared. Taking the refractivity of the mixture as unity, the following ratios were found:—

Hydrogen/mixture ..	1·5977 1·5957	Mean 1·5967
Helium/mixture ..	0·4513 0·4478	Mean 0·4495

The calculated values are—

$$\frac{(0{\cdot}04495 \times 20{\cdot}12)}{40{\cdot}72} = 22{\cdot}21.$$

$$\frac{(1{\cdot}5967 \times 20{\cdot}60)}{40{\cdot}72} = \frac{80{\cdot}87}{102{\cdot}99}.$$

Here the calculated value of the refractivity of the mixture is 3 per cent higher than the found value, while with air the calculated value is 0·35 per cent too low.

A third experiment was made, in which the "artificial air" was a mixture of 19·13 c.c. of carbon dioxide with 19·29 c.c. of oxygen, both gases supposed to be at 0° and 760 m.m. Again, taking the refractivity of the mixture as unity, we found the following ratio:—

Carbon dioxide/mixture	1·2450
Oxygen/mixture..	0·7525

The calculated values are—

$$\frac{(1{\cdot}2450 \times 19{\cdot}13)}{38{\cdot}42} = 61{\cdot}99.$$

$$\frac{(0{\cdot}7525 \times 19{\cdot}29)}{38{\cdot}42} = \frac{37{\cdot}78}{99{\cdot}77}.$$

Here, as with air, the total refractivity found is less than that calculated. It is true the difference is not great, but we are persuaded that it is real, for it considerably exceeds the error of our several determinations.

The case is not bettered if Lorentz and Lorenz's formula be substituted for Gladstone and Dale's. Using their formula, n^2-1/n^2+2, the calculated result is 99·72 per cent of that found for air.

The coefficient of compressibility of hydrogen is too small, while that of other gases, such as oxygen and nitrogen, is too great. The effect of mixing equal volumes of hydrogen and helium, each of which has too large a coefficient of elasticity, is to cause each to occupy twice the volume that they previously occupied, and to halve approximately the pressure for each. The pressure is therefore lower than it would be for an absolutely ideal gas, for each gas, hydrogen and helium. The sum of these pressures will accordingly be too low, or, transposing, the sum of the volumes will be too great. The opposite argument holds for air.

Now, in considering volumes we deal not merely with the co-volume, *i.e.*, the space occupied by the molecules, but also with the interstitial space inhabited by the molecules. But the refractive power, if Clausius's deduction from the formula of Lorenz and Lorentz is correct, is a function of the dielectric constant, and hence of the co-volumes of the gases. And here the discrepancy is more easily detected than by any determination of density. It must therefore be concluded that gases are not, as postulated by Dalton, indifferent to one another's presence, but that they modify one another's properties in the same manner as do liquids, though to a different extent. This mutual action at high pressures and small volumes modifies even the volume relations, as recently shown by Dr. Kuenen. And it must persist at low pressures and large volumes, though it may not always be possible to make measurements of pressure and volume accurate enough to lead to its detection. The refractivity, however, seems to be a means delicate enough to be used for this purpose.

HYSTERICAL CHEMISTRY.*

By Prof. H. CARRINGTON BOLTON, Ph.D.

The bizarre chemical theories, extravagant assumptions, and preposterous claims advanced in the writings of a certain small group of men having some knowledge of chemistry and an intense desire for notoriety seem, to a conservative student of contemporaneous science, to be products of disordered intellects; these pseudo-philosophers call themselves "Monists," and designate their peculiar doctrines as "Unitary Chemistry," but, from its emotional character, it may well be styled Hysterical Chemistry.

Their treatises generally have this feature in common; the authors begin with accepted facts and rational theories, leading to legitimate deductions, but at a certain point they allow their imagination to run riot, and thereafter the treatises follow most eccentric lines. The corner stone of their doctrine is the Unity of Matter, an hypothesis to which there is little objection *per se*, but they push it beyond legitimate bounds and graft on it corollaries of a most fantastic character. These authors spend very little time in laboratories, but claim to be working a revolution in chemistry and physics as well as in the sciences of philosophy and psychology by their publications; they complain that "official chemists" will not do justice to their novel theories. "Our views," writes one, "may appear strange to certain materialistic high priests of nineteenth-century science who imagine they know all and claim to explain everything, although they know and explain nothing," and he appeals for righteous judgment to "impartial men of science, lovers of Nature, who divine her infinite power and know how to decipher her language."

Some of these authors boast that their ultimate object is the transmutation of metals, and, together with certain devotees of theosophy, astrology, and occult science, they have formed the "Alchemical Association of France," an organisation whose workings and affiliations I have discussed elsewhere.

Singularly enough these hysterical chemists flourish chiefly in that enlightened nation that has given to science such men as Lavoisier, Gay-Lussac, Dumas, Berthelot, and Moissan. The chief apostles of this new

* Read to the Washington Section of the American Chemical Society, November 11th, 1897.

school are Louis Charles Emile Vial, F. Ch. Barlet, and François Jollivet-Castelot, and their guiding star is August Strindberg, a Swede. Their publications fall within the last twelve years, but they quote two authors whom they regard as pioneers: Louis Lucas, author of "La Nouvelle Chimie" (Paris, 1854) and Théodore Tiffereau, author of "Les Métaux sont des Corps Composés (Paris, 1855). The latter is, however, purely an alchemist. To the same school belonged Albert Poisson, who was founder of the "Hermetic Society of France, and died in 1894.* All are cordially endorsed by Paul Sédir, "Papus" (Dr. G. Encausse), and other occultists of high rank.

The Monist philosophers do not accept the elementary substances as chemical entities, and claim the unity of matter even though its forms appear diverse to our senses; they do not believe in identity, and are satisfied when analogies lead to a high degree of resemblance. They oppose these positive analogies to the "poetical and metaphysical concepts of official chemists," and as disciples of Aristotle they do not believe in a constructive resemblance of bodies, but only in the acquisition by bodies of given properties under certain conditions. They further claim that "all bodies and all forces have a common origin, and that chemists can derive one from another *at will*, no matter how diverse the phenomena observed, whether rarefaction or condensation, combination or mixture, attraction or repulsion, association or dissociation, addition or substitution." They are not bound by principles of pre-established harmony, of finality, or other vacillating conceptions; they expect the analogies to be clearly demonstrated, and if the accepted nomenclature disappears so much the better (August Strindberg, "Hortus Merlini; lettres sur la Chimie," Edition de l'Hyperchimie, Paris, 1897).

The Monists take for their motto: "Matter is one, everything comes from one, one is all." They claim for this doctrine great antiquity; it prevailed among the philosophers of India, Chaldea, and Egypt, and the alchemists of the Middle Ages represented it symbolically by a serpent biting its tail. The Monists extend the doctrine of evolution to the chemical elements, and assert that the infinitely small particles of primordial ether unite to form chemical atoms, which by self-evolution generate the diverse elementary bodies. Hydrogen, or perhaps helium, is the starting point. According to Tiffereau the evolution of the metals is accomplished by special microbes called sporules.

The views entertained by these philosophers are, however, diverse. M. Vial is not properly a Monist; he prefers to refer all matter to two types, one personified by hydrogen and the other by oxygen; according to him, "heat and cold, which are positive and negative elements represented by hydrogen and oxygen, are the universal agents, the cause of all chemical and physical phenomena, distinct and opposite entities." (L. C. Emile Vial, "La Chaleur et le Froid," Paris, 1884). And yet he inconsistently says, "Hydrogen is the divine principle of all things; by self-doubling it creates oxygen, which, being more condensed, and having generating power, becomes its second half." "Light results from the embrace of the primitive hydrogen with oxygen, and their union gives birth to water; hydrogen is the masculine element, oxygen the feminine, and water, which is the first two-fold type of nature, generates nitrogen by self-doubling. Created by water, nitrogen is succeeded by carbon, fluorine, chlorine, bromine, iodine, phosphorus, and finally sulphur."

In reviewing Vial's essay, Jollivet-Castelot remarks, "This masculine hydrogen and feminine oxygen are veritable monstrosities, in spite of the ingenuity of the hypothesis," and he points out that in attempting to construct a cycle of evolution of the chemical elements Vial is often obliged to alter their atomic weights to adjust them to the desired positions, though he brings forward no experimental proofs in support of these arbitrary changes. This complaint of one Monist by another is very amusing, for their disciples never use chemical tests to prove the presence or absence of a given element, but rely on analogies, the full meaning of which will appear later. Moreover the plaintiff in this case is one who gives the widest possible scope to his own amazingly free imagination.

In a recent work ("L'Amour dans l'Univers," Paris, 1896) Emile Vial explains his position in the following language: Unity is a duality of two opposite halves, just as an apple is composed of two half-apples. . . . . Unity is eternally divisible, and it is precisely this infinite divisibility that constitutes its duality." Applying this view to chemical atoms he writes: "A gaseous atom is a unity formed of two antagonistic principles, one material and the other immaterial."

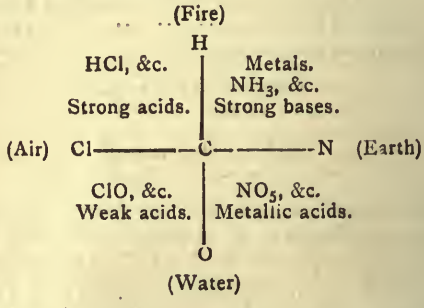
The mental operations of this transcendental philosopher are evidently conducted in four-dimensional space, and suggest the following catechism:—

What is Matter?—Never mind.
What is mind?—No matter.
What is spirit?—It is immaterial.

F. Ch. Barlet, said to be one of the most eminent occultists in France, and one of the founders of the "Université du Hautes Etudes," a school for cultivating esoteric studies, has published an essay entitled "La Chimie Synthétique" (Paris, 1897) which exhibits the peculiar characteristics of hysterical chemistry. Barlet rehearses at length, and with some skill, the growth of chemical theories from the dualism of Berzelius to the Periodic Law of Mendeléeff, and he gives preference to Sir William Crookes's method of representing the elements in order of their atomic weights by a spiral; this graphic construction he improves (?) by changing the spiral into a horizontal plane, which he then divides into four equal parts by two sectors crossing at right angles. The chemical elements falling within these segments he finds correspond to the four elements of ancient philosophy,

Fire	Air
Earth	Water

and on this correspondence he bases all his subsequent ratiocination. It would not be profitable to follow in detail the mental vagaries which finally lead Barlet to present the following scheme.



Following the opinions of P. Leroy (Eudiste, "Essai sur la Synthèse des Forces Physiques," Paris, 1892, 2 Nos.), he imagines the ether of physics immersed in a medium still more subtle called "Eon." A mixture of ether and eon is the protyle of Crookes and the Astral Light of theosophy; in this medium the four elements are formed under the influence of quintessence, which after all is nothing but eon penetrating ether! Barlet

* Albert Poisson's principal works are: (1) "Théories et Symboles des Alchimistes" (Paris, 1891. (2) "Cinq Traités d'Alchimie des Plus Grands Philosophes." Traduit du Latin (Paris, 1890); Nicolas Flamel, Paris, 1891.

concludes his extraordinary disquisition with the following lucid summary:—

The principal doctrines of this philosophy are "the periodical, continual evolution of the subtle into the dense, of eon into ether, of quintessence into matter, of the divine Fire attracted by the desire of Astringency, of the Spirit called by Matter, of the Being evoked by Nothingness; the formidable hierarchy of creatures which extends between the two poles of the Infinite, the cosmic life traversing their development as the fulfilment of that ineffable Mystery which manifests itself in the Inexpressible Absolute!"

"I smiled and said it must be so,
In fact I thought so then,
For there was much I did not know
Of the Whatness of the When."

"All that exists lives, all that exists is evolved and transforms itself" is one of the favourite tenets of the Monists, who designate it by the term "Hylozoism." M. Jollivet-Castelot, a member of the "Groupe Indépendent d'Etudes Esotériques," is the chief exponent of this doctrine, having devoted to it an entire volume besides chapters in other works. ("La Vie et l'Ame de la Matière; Essai de Physiologie Chimique," Paris, 1894. "L'Hylozoisme; L'Alchimie; Les Chimistes Unitaires," Paris, 1896. "Comment On Devient Alchimiste," Paris, 1897.) That which is commonly called inert or dead matter (metals, minerals, elementary bodies, even the physical atoms), according to Hylozoistic Monists, is not dead, but is possessed of life, analogous to plants and animals, but less active and conspicuous. Thus the three kingdoms of nature, animal, vegetable, and mineral, are brought within the influence of evolution. Some of the extremists go so far as to endow the atoms with feeling, instinct, and will (Fouillée, "Revue des Deux Mondes," Oct. 16th, 1886, p. 895), and maintain that the atom plays the same rôle in chemistry as the cell-germ in physiology. One element generates another by polymerisation, scission, agglomeration, substitution, condensation, &c., communicating to it, *by heredity*, certain properties; these properties, however, are combated by the tendency to variation, the sexual selection of the chemical elements, and perhaps by natural selection acting in the chemical world as in organised beings." The author cited (Jollivet-Castelot) writes of the individuality of mineral beings as proved by their choice of colours, and of their "souls," which, however, are inferior to the souls of plants and animals. "Admitting a human spiritism, there must exist a vegetable and a mineral spiritism, for we know that the entire universe is animated by an evolutive Intelligence organising Matter and condensing Energy." "I will not go so far," writes Jollivet-Castelot, "as to affirm that electricity is the soul, ... but I venture to say that electricity excites the spiritualistic phenomena, accompanies them, and serves perhaps as an intermediary between conscience and organised matter." Applying these extraordinary views to common physical and chemical phenomena, the Hylozoist states that "Water of crystallisation constitutes a kind of mineral respiration, demonstrating in a special way the Life of Matter. The substance has a positive need of water, absorbs it, utilises it, expels it, and submits to an evident motion of inhalation and exhalation."

This bizarre doctrine is opposed by its disciples to the materialistic theories of scientists who would reduce mental activity to automatic mechanism, and they cite approvingly the profound epigram of Aristotle:

"All motion is a kind of appetite,"

as well as the saying of Liebnitz:

"Nothing in nature is dead."

Great antiquity is claimed for this philosophical system. It served as a foundation for ancient Oriental religions; the priests of Brahma and of Buddha, the hierophants of Chaldea and of the sacred temples of the Egyptian goddess Isis, all maintained that the universe is living, animated, and evolved. Moreover the alchemists of the Middle Ages and eminent physiologists of ancient and modern times, have uniformly supported these opinions. In a few years the scientific world will doubtless be entirely converted to Hylozoism.

A certain number of these hysterical chemists are devoted to theosophy, and apply its principles to the more practical science; they claim that the true adept has no need of retorts, furnaces, or chemical menstruums, but he is capable of accomplishing the union and separation of atoms by the force of his will and the power of his magical faculties.

(To be continued).

LABORATORY NOTES.

Asbestos—Combustion Furnaces.

By H. JERVIS.

It is a trite observation that a body is valuable as it possesses hardness, weight, stability, or other properties desirable for a set purpose. Asbestos possesses properties so varied, and so subject to designed modification, that its limited use in the laboratory may well excite remark

The most useful property is its comparative stability at high temperatures. This property is all the more valuable because, before heating, the asbestos may be moistened with water and worked into any desirable shape as easily as a piece of clay. Such models when dried, but not ignited, may be roughly handled without detriment. Other of its properties are indifference to sudden heating or cooling, lightness, and toughness. Two other properties, which have frequently to be considered negative ones, are the tendency to laminate when subjected to pressure and the rottenness after strong ignition. It does not seem unreasonable, however, to hope that these properties may be modified.

To illustrate the value of this material we will mention a few of the forms in which it has served us in the laboratory, some of its common uses, and then some new uses, along with a few forms of apparatus its use makes possible.

As fibre, asbestos is used everywhere for filtering liquids, plugging furnace tubes, &c. As woven cloth, it is useful for wrapping round the necks of hot water washbottles, though in this respect it is inferior to sheet cork, except that it lasts much longer; the threads, which are easily detached from the piece, are used as string, where hemp or even wire are not permissible; this form is very strong, and of course does not laminate. Millboard, useful kinds of which may vary from the thickness of stout paper to half an inch or more, is used for laying over muffle bottoms, coating porcelain boats so that they may not stick to more fusible surfaces, wrapping round combustion tubes after cutting (if needful) an opening through which to watch the operation.

Two other uses are so intimately connected with the modifications to be described, that they may be mentioned separately.

White (Chemical News, xliv., 65) describes an asbestos stopper made by separating the asbestos into fine threads, moistening with water, twisting into the cylinder of a steel mortar, and pressing in a vice. Here the tendency to laminate is much lessened by using the long threads, and the stoppers are serviceable for a few times, but they are too fragile to bear the pull and push of constant use. As an adjunct to indiarubber, we have used a thick washer of asbestos millboard fitted to the smaller end of the stopper, and kept in position by turning the ends of the glass tube outwards. The millboard contains oily matter, which may be removed by simply igniting in a muffle. The washers are much less subject to lamination if they be

soaked in some decomposable metallic salt before ignition. A mixture of chromic and sulphuric acid gives good results, but the washers must be only just soaked, not digested.

Stoke (CHEMICAL NEWS, lvii., 150) suggested that furnace tiles, if cut from asbestos millboard, would form a lighter, hotter, and less breakable covering for a combustion-tube than those made of fire-clay. The suggestion has much merit. In practice, however, the teeth of the tiles made "rotten" by heat are readily damaged during the unavoidable putting on and off which ofttimes attends combustions.

It may be taken as a general rule that, when intended for exposure to heat and handling, an asbestos model should be made as free as possible from edges and corners. In keeping with this dogma we recommend the shape shown in Fig. 1. Its position on the furnace is

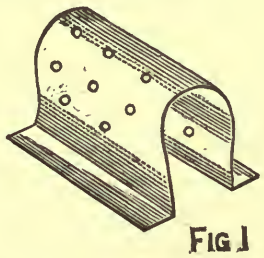


FIG 1

sufficiently obvious. It is necessary only to describe its construction.

A piece of millboard (⅛"×4"×10") is perforated with glycerined cork-borers, as shown. It is then nicked about an inch from each short end, and laid in water until quite saturated. Bend from the nicks through 90°, and then lay the centre of the asbestos over a bottle (2" diam.), and bend it to the bottle's shape. Very little force is necessary and very little should be used, or the holes will be closed somewhat. Remove the bottle, press the ledges of the model on to the table, and amend irregularities of shape. The drying may best be done by removing the cover to its furnace, setting it in position on the supports, and pressing it well thereto. When quite dried by the lighted furnace it will be found to have retained its shape and to need a knife to separate it from the iron supports.

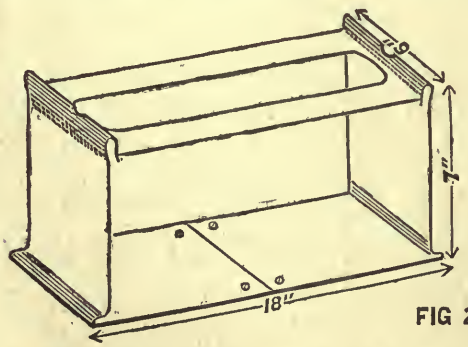


FIG 2

Our experience has been that the temperature is greater with these covers than with fire-clay tiles. When the temperature needs to be unusually high, a second larger cover, but similar in other respects, is placed over the first, and can be moved along the tube at will.

In appearance and weight the new cover is a great improvement. To satisfy curiosity it was found that the twenty-four tiles previously used, weighing 13 lbs., had been replaced by three covers weighing 1 lb. This of itself is merely a detail when the ordinary form of furnace is satisfactorily at work, but it opens the way to the general adoption of a lighter form of furnace.

Combustion furnaces of thin sheet iron have been previously described. We submit the form shown in Fig. 2. It is represented screwed to the table. It was made from a single sheet of mild steel 5 feet long and about one thirty-second of an inch thick, during a meal-time (1½ hours) in the laboratory. The outer pieces are not cut away, but nicked merely and bent under. The centre-piece was cut out with a sharp chisel, and the tube nests made with a file. The bending was done chiefly over table-edges and cupboard-doors. When used with the afore-mentioned covers it forms an apparatus both cheap and effective.

A common support for combustion-tubes used temporarily is a Y-shaped stiff wire, sliding in a wooden base. Such an arrangement may be very readily converted into an efficient combustion-furnace, having the appearance shown in Fig. 3.

The arrangement supporting the tube and cover is made from a piece of steel, circular in section and tapering to the ends, to which are attached the wires. Such pieces with threaded holes are returned to steel-works in large quantities along with "spindle scrap"; I believe they are spindles.

As we have become so mixed up with combustion-furnaces, it may be as well to use its accessories to illustrate some further uses of asbestos.

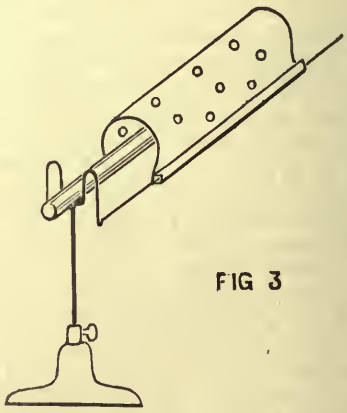


FIG 3

Tubes of asbestos are out of the question at present. The Y-shaped movable tap for Bunsen burners, giving a long flame, may very easily be made from asbestos, and, as they need only be dried, they stand hard wear for a long time. After soaking the tips in suitable solutions they show flame colourations very well. Two pieces of thin millboard are cut, wetted, and shaped; a thin slip of glycerined wood or glass placed between the upper end preserves an even opening, and may be readily removed when the rest is dry. To fit it on to the burner it is necessary only to wet the circular end, place it in position, and press it.

The furnace cover serves very well, when suspended by one edge, for augmenting the heat of a blowpipe flame when working hard combustion-tubing. It is possible thus to make bulbs and bottles from material which with the unaided flame could be drawn out only with difficulty after prolonged heating.

There are other uses of asbestos peculiar to personal occupations, and of no general interest. One need not grow hyperbolic in its praise. When its obedience to one's fingers is once understood it becomes more interesting than a kindergarten lesson to shape the material to its manifold uses.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 16th, 1897.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. James C. Philip, Edward Rosling, and Frank T. Addyman were formally admitted Fellows of the Society.

The President announced that the following had been recommended by Council for election as Foreign Members, to be balloted for at the next meeting, January 20th, 1898.

Prof. Remsen, Baltimore, U.S.A.; Prof. Troost, Paris; Prof. Moissan, Paris; Prof. Raoult, Grenoble; Prof. Ostwald, Leipzig; Prof. Curtius, Bonn; Prof. Mensutkin, St. Petersburg; Prof. Markownikow, St. Petersburg; Prof. Arrhenius, Stockholm; Prof. Waage, Christiania; Prof. Franchimont, Leyden; Prof. van der Waals, Amsterdam; Prof. Spring, Liége; Prof. Körner, Milan.

Certificates were read for the first time in favour of Messrs. E. L. Allhusen, B.Sc., Geological Survey, Perth, W.A.; B. S. Bull, M.A., B.Sc., Ph.D., 49, Devonshire Road, Greenwich; T. H. Hills, 6, Eliot Park, Blackheath; J. E. Miller, Holmoor, Patrington, Hull; G. T. Morgan, 35A, Russell Road, Kensington, W.; W. E. Moss, B.A., Burnthwaite, Bolton; H. Poole, 323, W. 34th Street, New York; W. Richards, Old Elvet, Durham.

The following papers were read :—

*126. "*Stereochemistry of Unsaturated Compounds.* Part I. *Esterification of Substituted Acrylic Acids.*" By John J. Sudborough and Lorenzo L. Lloyd.

In order to determine whether there is any general rule applying to the esterification of unsaturated acids, similar to those discovered by Mensutkin for fatty acids, and by Victor Meyer and Sudborough for aromatic acids, the authors have investigated the following acids: cinnamic acid, allocinnamic acid, atropic acid, ortho-, meta-, and para-nitrocinnamic acids, α-bromocinnamic acid, α-bromallocinnamic acid, two β-bromocinnamic acids, two α-β-dibromocinnamic acids, α-β-dichlorcinnamic acid, α-β-di-iodocinnamic acid, α-cyanocinnamic acid, α-cyano-meta- and α-cyano-ortho-nitrocinnamic acid, α-phenylcinnamic acid, α-phenylallocinnamic acid, six α-phenylnitrocinnamic acids, triphenylacrylic acid, α-β-di-iodoacrylic acid. Half a grm. of each acid was boiled for an hour with 10 c.c. of a 3 per cent. solution of hydrogen chloride in methylic alcohol, and the amount of ester formed determined in the usual manner.

The authors draw the following conclusions from the results which they have obtained :—

(1) Unsaturated acids of the types,

$$H(Y)C:C(X)CO_2H \text{ and } Z(Y)C:C(X)CO_2H,$$

yield but small amounts of ester when treated in the manner described.

This furnishes a ready method for distinguishing stereoisomeric acids.

(1) $H(Y)C:C(X)CO_2H$ and (2) $H(Y)C:C(CO_2H)X$.

As acids of the trans-type (1) are esterified with difficulty, and acids of the cis- type (2) with ease by the above method, it is probable that the method can also be used for separating mixtures of such acids, in very much the same manner that diortho-substituted benzoic acids can be separated from their isomers.

(2) An α-substituted acrylic acid, $CO_2HC(X):CH_2$, is more difficult to esterify than a β-substituted acid, $CO_2HC(H):CHX$.

(3) In certain substituted cinnamic acids, a nitro-group in the ortho- position appears to have a retarding influence. The results obtained are completely in accord with those published by Anschütz (*Ber.*, 1897, xxx., 2652) whilst the present work was still being carried out.

The constitution of camphoric acid is discussed in the light of the results contained in the paper.

The authors think it desirable to carry out similar researches with substituted acids; they have already found that dibromosuccinic acid, phenyldibromopropionic acid and its nitro-derivatives, yield but little ester when boiled for an hour with a 3 per cent. solution of hydrogen chloride in methylic alcohol. Several new methylic esters have been obtained, and are described in the paper.

*127. "*Formation and Hydrolysis of Esters.*" By John J. Sudborough, Ph.D., D.Sc., and Martin E. Feilmann, B.Sc.

From the researches of Mensutkin (*Annalen*, 1879, cxcv., 334, 1879, cxcvii., 193) on the esterification of fatty acids, of Victor Meyer and Sudborough (*Ber.*, 1894, xxvii., 510, 1580, 3146) on substituted benzoic acids, and of Sudborough and Lloyd (preceding abstract) and Anschütz (*Ber.*, 1897, xxx., 2652) on unsaturated acids, the authors consider it proved beyond doubt that stereochemical influences play a most important part in the esterification of an acid by means of an alcohol and hydrogen chloride. Researches by Kellas (*Z. Physik. Chem.*, 1897, xxv., 221) on the esterification of monosubstituted benzoic acids, and of Sell (*Trans.*, 1897, lxxi, 1070) on substituted pyridinecarboxylic acids also support the same conclusion. In the benzoic and acrylic acid series, the chemical nature of the substituting groups has but little, if any, influence on the retardation of esterification. CH_3, F, Cl, Br, I, NO_2, OH and CO_2H groups all act in the same manner; the radicle weight or volume, however, affects the retardation to a certain extent (Meyer, *Ber.*, 1895, xxviii, 1259, and Kellas, *loc. cit.*).

One would therefore conclude that in the fatty series, too, the chemical nature of the substituting groups would have but little, if any, apparent influence. A tertiary fatty acid, however, such as trimethylacetic acid, yields but little ester when heated with alcohol (Mensutkin), whilst the similarly constituted trichloracetic acid is most readily esterified, in fact, much more readily than acetic, mono- or di-chloracetic acids (Lichty, *Am. Chem. Journ.*, 1896, xviii., 590). This difference in behaviour we can only attribute to the enormous increase in strength of the acid.

	K.		K.
(1) Acetic acid	0·0018	(3) Dichloracetic acid	5·14
(2) Chloracetic acid	0·155	(4) Trichloracetic acid	121·0

Lichty's researches show that these four acids follow exactly the order given above as regards the ease with which they are esterified. The amounts of ester formed at the end of any given time by no means bear the same ratio to one another as do the affinity constants of the corresponding acids.

	After 1 min.	1 hour.	2 hours.	
Chloracetic ..	1·78	41·89	57·33	per cent
Dichloracetic ..	4·56	56·49	62·34	,,
Trichloracetic ..	9·99	59·39	66·18	,,

It would appear then that some other factor is introduced which tends to hinder the formation of the esters, and this factor the authors consider to be the stereochemical influence of the chlorine atoms. The general conclusion drawn is that in the conversion of an acid into its ester by the action of an alcohol, either with or without hydrogen chloride, the rate of esterification is determined by two factors :—1. The configuration of the acid; in other words, the presence of substituting groups situated close to the carboxylic group, which always tend to hinder esterification. 2. The strength of the acid as determined by its affinity constant. In most of the cases which have been more closely studied, the first factor is the more prominent, and obscures to a large extent, the

influence of the second factor. In exceptional cases, however, namely, in acids the strength of which has been enormously increased, the second factor becomes the more prominent, and the influence of configuration is cloaked. In all cases, however, we must suppose the two factors to be in force, and it is only in acids which have the same affinity constant that the true effect of stereochemical influence can be looked for.

No general systematic study of the rate of hydrolysis of esters appears to have been attempted. Victor Meyer (*Ber.*, 1895, xxviii., 1263) formulated the generalisation that those esters which are the most difficult to form are also the most difficult to hydrolyse. This view was also held by Wegscheider (*Ber.*, 1895, xxviii., 2536) and Brühl, but according to the more recent investigations of Kellas, this generalisation is not strictly correct. Kellas (*loc. cit.*) stated the rate of hydrolysis of the methyl salts of mono-substituted benzoic acids by means of alkali. He found that in any given series the ortho-compound is always the most difficult to hydrolyse, the para- occupies an intermediate position, and the meta- is most readily hydrolysed (with the exception of the nitro-compounds). It is stated, however, that methylic orthonitrobenzoate is much more readily hydrolysed than methylic orthotoluate, although the nitro-ester is formed much more slowly than the toluate. This and similar results noted by Kellas, for example, the fact that methylic benzoate is difficult to hydrolyse, can be accounted for by the introduction of the affinity of the acid as a factor. For orthonitrobenzoic acid K=0·616, for orthotoluic acid K=0·012, and for benzoic acid K=0·006. The results obtained by Hjelt (*Ber.*, 1896, xxix., 1864) on the hydrolysis of the ethylic salt of substituted malonic acids also lead to the same conclusions. They indicate that here, also, the rate of hydrolysis does not depend merely on the stereochemistry of the ester molecule. If the affinity constants are taken into consideration, the obstruction due to the substituting groups is much more pronounced (with the exception of ethylic allylmalonate). Investigations by the authors on the hydrolysis of the ethylic salts of acetic, methyl-, dimethyl-, and trimethylacetic acids by the aid of sodium hydroxide, prove that here, where the affinity constants of the acids vary but little—acetic acid K=0·0018; propionic acid K=0·00134; isobutyric acid=0·00144, and trimethylic acetic acid (unknown, but at any rate very small, since the salts of this acid are extremely unstable)—the rates of hydrolysis are what would be expected from the introduction of the substituting groups—

	Hours.	0·25	0·5	1	1·5	2·5	3	4	4½	8	10	22·5	70	
Ethylic acetate		19·6	28	42	—	—	66	—	—	82·6	85·4	—	—	per cent.
„ propionate		14·4	19·6	—	35·6	—	50·8	—	61·2	—	—	—	—	„ „
„ isobutyrate		5·2	7·2	11·4	—	19·2	—	—	—	—	—	61	—	„ „
„ trimethylacetate..		—	—	—	2·4	—	—	6·8	—	8·8	—	—	19·6	„ „

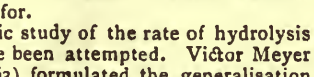
With the esters of chlorinated and brominated acetic acids, the reverse is true, and all are decomposed much more readily than ethylic acetate itself. Comparative experiments with these esters are being undertaken by the authors.

The general conclusion arrived at is, therefore, that in the hydrolysis of esters by the aid of an alkali the same two factors operate as in esterification. The strength of the acid which is formed by the hydrolysis of the ester seems, however, to play a more important part than it did in esterification, and this accounts for the fact that it does not always follow that esters which are most readily formed are the most readily hydrolysed.

Other factors are apparently [illegible] duced when esters are hydrolysed by the aid of hyd[illegible]uric acid, as it has been proved that esters by no me[illegible]s arrange themselves in the same order when hydrolysed by an alkali as when hydrolysed by an acid (Hemptinne, *Z. physik. Chem.*, 1894, xiii., 561; Löwenherz, *ibid.*, 1894, vi., 389; Van Dyken, *Rec. Trav. Chim.*, 1895, xiv., 106). The authors consider that these generalisations can be proved or refuted only by a much more careful study of the hydrolysis of numerous series of esters. They themselves intend investigating the ethylic salts of substituted (alkylated) succinic acids, as the strengths of these acids differ but little, and therefore the results obtained should throw light upon the retarding effect of different alkylic groups.

Discussion.

Dr. Hewitt said that the fact that hydroxylfluorone-carboxylic acid,—



yields scarcely any ethyl ester, even after prolonged boiling with 9 parts by weight of ethyl alcohol and 1 part of concentrated sulphuric acid, is easily explicable in the light of Dr. Sudborough's work. Hydroxylfluorone-carboxylic acid is a tri-substituted acrylic acid, and hence should not easily esterify. On the other hand, Victor Meyer showed that triphenylacrylic acid,—

$$Ph_2C:C(Ph)\cdot CO_2H,$$

yielded an ester by prolonged boiling with methyl alcohol and a stream of hydrogen chloride. Under similar circumstances, triphenyl acetic acid, $(C_6H_5)_3CO_2H$, furnished very little ester.

Dr. Shields called attention to the numbers, quoted by the authors of the papers, representing the percentage amount of etherification after one minute, one hour, and two hours, and remarked that, whereas all the limiting values were approximately the same after sufficient time had elapsed, a considerable difference existed between the numbers when the amount of transformation was measured after the lapse of only one minute. If it had been possible to obtain the corresponding values after one second, he thought the difference would have been still greater, and that in any serious attempt to study parallelism between the velocity of etherification and the affinity constants of the acids, it would be necessary to determine the velocity constant of the reaction or the initial rate of etherification.

*128. "*A New Method of Determining Freezing-points in very Dilute Solution.*" By Meyer Wilderman, Ph.D.

The chief condition for obtaining correct determinations of the freezing-point is the establishment of equilibrium between the solid and the liquid part of the heterogeneous system. Starting from the properties of "perfect" equilibrium, and from the equations for velocity of ice-melting, ice-separation, and Newton's equation for cooling, all the conditions necessary for a successful experiment, previously laid down empirically by the late P. B. Lewis and then by the author, are now deduced from theoretical considerations. It is shown how to arrange the equilibrium with an accuracy of 0·000002—0·00006°, and even greater. The freezing-point method, which has been hitherto a conglomeration of empirical rules, is thus placed on a physico-mathematical basis, and the experimental error of all previous methods can be calculated. The second important point in a freezing-point method is a correct and very detailed knowledge of the registering instrument. A very careful study of the errors of mercury thermometers has been made for a long time, and an account of this is given. This paper is a continuation of that by P. B. Lewis (*Trans.*, 1895, lxvii., 1).

Discussion.

Mr. Pickering expressed his disappointment that the

author had not made any statement as to what his "new method" was. All that he had given was a summary, in the form of an equation, of the various inaccuracies inherent in freezing-point determinations generally. These inaccuracies were well known, and it was of great importance that they should be reduced to a minimum; but it was impossible to say whether the author's new method succeeded in doing this or not until a description of the method was given.

Dr. Shields remarked that the literature and controversies on the vexed question of the accurate determination of the freezing-point of dilute solutions would already fill a large volume. Since the subject was one of great importance in connection with the modern theory of solutions, any new contribution which was likely to lead to a final settlement of the conflicting views was welcome. He regretted that want of time had prevented Dr. Wilderman from giving a fuller account of his paper, but the method of attack adopted by the author was undoubtedly a step in the right direction, and he thought that the study of the time reaction and of equilibrium in freezing solutions would lead, if it had not already in Dr. Wilderman's hands led, to important advances.

Dr. Wilderman, in reply, stated that methods were given in the paper for obtaining the separated ice in fine films throughout the liquid. In answer to Mr. Pickering, he said that the value of the equations he laid down was, that by them the errors due to equilibrium in the methods of other investigators could be estimated, and their results re-calculated. As an illustration, one of the most accurate of the recent methods was re-calculated, and its error found to be 160 times greater than his own. He had presented, for the first time, the physico-mathematical theory of freezing-point determinations in such a form that future experimenters could arrange with ease the equilibrium to any degree of accuracy required.

*129. "*A possible Basis of Generalisation of Isomeric Changes in Organic Compounds.*" By Arthur Lapworth, D.Sc.

In this paper the author points out that many isomeric changes, hitherto regarded as belonging to different types, may he formulated as special cases of a general form, which may be expressed by the reversible equation—

$$R_\alpha M \cdot R_\beta : R_\gamma \rightleftarrows R_\alpha : R_\beta \cdot R_\gamma M,$$

representing a labile group moving from an α-atom to a γ-atom, the necessary re-arrangement of single and double bindings taking place between the three atoms R_α, R_β, and R_γ. A conventional "mechanical" representation of the change is given for the special case where R_α, R_β, and R_γ are carbon atoms.

Examples, for the most part derived from "tautomeric" and "desmotropic" substances, such as acetoacetic ether, cyanic acid, nitroso-compounds, &c., are shown to be of the above type.

Extensions of the above special form are deduced, and the general conclusion is arrived at, that in a chain of alternately singly- and doubly-linked atoms, either (1) a labile group may become successively attached to alternate atoms, or (2) an exchange of labile groups in γ- (*i.e.*, meta-) positions may occur. These deductions are shown to be confirmed by the behaviour of benzenoid compounds, &c, the fully justifiable assumption being made that benzenoid compounds may act as if possessing Kekulé's formula. Special reference is made to nitrophenol, orthohydroxyazobenzene, the sulphonic derivatives of aniline and of β-naphthol, and also to the changes of methylaniline into paratoluidine, and of hydrazobenzene into benzidine, which are all shown to exhibit changes in complete accordance with the author's views.

Further modification of the general formula for the case where R_β and R_γ are singly, instead of doubly, linked, is shown to lead to the form—

$$R_\alpha M \cdot R_\beta \cdot R_\gamma \rightleftarrows R_\alpha : R_\beta + R_\gamma \cdot M,$$

which represents on the one hand the great majority of simple molecular decompositions of organic compounds, and on the other the formation of the ordinary addition products from unsaturated substances. The production of substitution derivatives, &c., by successive addition and isomeric change (compare Armstrong, *Trans.*, 1887, li., 258), as well as some simple cases of hydrolysis, are then discussed.

From the last formula the following type is shown to be at once derivable:—

$$R_\alpha \cdot M + R_\beta \cdot R_\gamma \rightleftarrows R_\alpha \cdot R_\beta + R_\gamma M,$$

which represents the ordinary process of substitution in saturated compounds (compare Armstrong, *loc. cit.*, and Williamson, "Theory of Etherification, 1851).

With the help of the foregoing principles, the author shows that the production of meta-di-derivatives from certain mono-derivatives of benzene may be consistently explained on the basis of Armstrong's suggestion (*loc. cit.*) that in such mono-derivatives addition of the acting agent to the side group precedes substitution. Further, this assumption at once explains the replacement (by a substituting group) of side groups, which otherwise afford meta-derivatives.

Some apparent exceptions to the foregoing principle are next dealt with, and it is shown that little difficulty exists in relegating to the above type the production of, for example, pinacolines from pinacones, acetanilide from acetophenone-oxine, benzilic acid from benzil, &c., on suppositions which, for the most part, the author has not been the first to make, and which mostly involve the intermediate production of ring-compounds.

It is further shown that the following type of change is possibly, but by no means necessarily, independent of the above, viz.,

$$R_\alpha M \cdot \overset{\cdot\cdot}{R_\beta} \rightleftarrows R_\alpha : R_\beta M$$

(where $\overset{\cdot\cdot}{R_\beta}$ represents an atom possessing a "residual affinity" of two units), and a possible method of harmonising this with the other type is discussed in detail.

Finally, it is pointed out that, although a brief dissociation between the labile group and its attached atom must be assumed in order to account for the above changes, cases involving electrolytic dissociation or partial destruction of the labile substance necessarily involve probable changes other than an $\alpha\gamma$-isomeric change, and should therefore be as far as possible avoided in investigating the applicability of the foregoing generalisation.

Discussion.

Dr. Wynne regretted that the author, in reading his paper, had thought it more important to enumerate the various well-known cases of tautomerism, than to give the explanation he had devised to account for this property. So far as could be gathered the author sought to connect those reactions in which a single radicle is transferred from one to the other of positions relatively 1:3 accompanied by a change of structure in the chain, with those in which mutual exchange of radicles in positions relatively 1:3 is brought about without any structural rearrangement. It was difficult to see wherein the analogy lay, but even if the author's contention were adopted, it was open to question whether anything had been thereby gained. The usual statement that ortho-, or para-, or both di-derivatives result from compounds of the phenylsulphamic acid type expressed the facts at least as clearly as the author's emendation, wherein the reaction is represented as being brought about by the radicle moving from any given position to the next but one. What was to be desired was an explanation of the cause of the mutual transference, not a re-statement of the fact of its occurrence.

The author's view of the formation of metanitrobenzene-sulphonic acid surely needed more explanation than the reaction for which it was put forward to account, and the same might be said of the arguments brought forward to explain the production of metasulphonic acids from aniline derivatives. A striking case of the production of such acids is ezhibited by dimethylaniline, which with ordinary sulphuric acid gives the para-, whilst with fuming sulphuric acid, a mixture of the meta- and para-sulphonic acids is obtained. Yet, according to the author's views, the meta-sulphonic acid should be the sole product in either case, since he considers that compounds of the phenylsulphamic acid type—which dimethylaniline can form—give rise to metasulphonic acids.

Again the order in which isomeric sulphonic acids seem to be formed in the case of β-naphthol had been adduced by the author in support of his views, but it was not difficult to quote cases in which it appeared to be inapplicable. Erdmann had shown that 1 : 4-, 1 4'-, and 1 : 3'-α-naphthylaminesulphonic acids are the products of the sulphonation of α-naphthylamine, and it was not easy to see how the production of the last-named and most stable of these acids could be accounted for by the author, even if his views did not beg the question of the mode in which isomeric sulphonic acids are formed, as reference to Erdmann's paper would show.

He was, moreover, unable to follow the author in tracing an analogy between the changes involving the production of ethylene from ethyl bromide, and of ethyl bromide from ethylene on the one hand, and those occurring in tautomeric compounds on the other; an analogy, that is, between reactions involving scission of the chain, and those in which none occurs. Markownikow's rule embraced what is known of such reactions, and the author's re-statement of some of the facts did not seem to add to, or explain, that well-known summary.

Professor Collie said that this generalisation of Dr. Lapworth's appeared to him to be one of great importance. Any simple rule that would explain not only all cases of isomeric change amongst paraffinoid as well as amongst benzenoid derivatives, but also the hydrolysis of esters, the decomposition of diazo-compounds, the formation of meta-derivatives, &c., &c., was one which certainly claimed the attention of chemists. Moreover, it received much support from a stereochemical point of view; and if Dr. Lapworth's first equation be allowed, then the rest of the argument was a clearly worked out, logical deduction.

Dr. Kipping agreed with the last speaker, that the paper under discussion was one of great interest and importance. Starting from a simple case of tautomeric change, by an ingenious and logical application of views already widely accepted, Dr. Lapworth had attempted to account for, and to bring into line, a very large number of cases of isomeric change, which before seemed to be complex, obscure, and not related to one another in any way. If this generalisation were possible, as it certainly seemed to be from the formulæ and explanations which Dr. Lapworth had advanced, his paper deserved, and would no doubt receive, the careful consideration of chemists.

Mr. A. G. Bloxam asked whether, in the event of such tautomerism as that referred to by Dr. Lapworth occurring in di-substitution products, the second group would exert any preventive action on the wandering of the first group. Thus, supposing that a sulphonic group tended to wander into the next following γ-position, which, however, was already occupied by another group, would such a state of affairs determine the non-existence of a tautomeric form?

Dr. Lapworth, in replying, regretted that the time at his disposal had prevented him from saying all he had wished. He had tried, in the first instance, to show that a great many isomeric changes, including those of elimination of two groups attached to contiguous carbon atoms and also of most changes in benzenoid compounds, might be written in a form derived from that representing the relationship between the two forms of simple tautomeric substances, and had shown in the paper that they might be represented on exactly similar stereo-chemical bases. The latter he had omitted to give in reading, as it involved the introduction of the usual hypothetical space-relationships of carbon atoms and the idea of dissociation as distinct from decomposition, whilst the paper intended to call attention to what appeared to be a general type of change, logically deducible from a well-known form.

With regard to the production of benzenoid substitution derivatives, he had already pointed out that, as a rule, where substitution in the benzene nucleus undoubtedly occurs, ortho- and para-derivatives are the chief products, and that this fact, as also the question of the stability of a particular benzene derivative, must depend on some principle not intimately connected with the mechanism of isomeric change. A change, analogous to that of compounds of the aniline hydrogen sulphate type would afford meta-derivatives, and evidence of this is afforded by the production of metanitraniline when aniline nitrate is treated with cold sulphuric acid; the production of ortho- and para-derivatives may then be due either to direct substitution in the ring, or to isomeric change of compounds of the phenylsulphamic acid or methylaniline type. Hence the formation of any particular acid from aniline, dimethylaniline, α- and β-naphthylamines, &c., is not difficult to account for, although the exact details of the production, or any one of them, would require a special discussion.

The convenience of employing the above formulæ and the apparently very general applicability of the type of change to which the author desired to draw attention, would only be understood when it was applied to cases which, as the author shows in his paper, are difficult to discuss on the usual bases.

In reply to Mr. Bloxam, the author said that the paper dealt with cases in which the γ-position was already occupied, and in the special case alluded to, the author's view made it clear that no entirely preventive action would be exercised, and this would appear to be in accordance with known cases.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxv., No. 21, November 22, 1897.

Influence of Temperature on the Rotatory Power of Liquids.— Ph. A. Guye and Mlle. E. Aston. — The authors find that there are a few exceptions to the general rule that the specific rotatory power of a liquid diminishes progressively, with an increase of temperature, without any sudden variation when the liquid passes to the gaseous state. The most interesting case up to the present appears to be amylic alcohol, in which the rotatory power at first diminishes as the temperature rises, only to increase again as the boiling-point is reached.

On Chlorocyanamide, $C_3N_3(NH_2)_2Cl$. — Paul Lemoult. — When cyanuric chloride is digested in the cold with an ammoniacal solution the latter disappears completely,—a salt of ammonia is formed and a white powder deposited, very slightly soluble in water: this is monochlorised cyanuramide, the chlorocyanamide of Liebig. This impure product is dissolved in a large quantity of boiling water; on cooling, the filtered solution deposits fine needle-like crystals of the pure substance. Its molecular heat of combustion, at a constant volume, is 401·3

cals., and at a constant pressure 400·3 cals. The molecular heat of formation at constant pressure is therefore 25·6 cals.

Contribution to the Study of the Nitrification of Soils.—Th. Schlœsing, jun.—This paper will be inserted in full.

No. 22, November 29, 1897.

On a New Method of Preparing Carbides by the Action of Carbide of Calcium on the Oxides.—Henri Moissan.—Besides its curious action on water, carbide of calcium acts as a powerful reducing agent, and, thanks to this property, can furnish a number of new compounds by double reaction, but only when in contact with the body in a liquid state, or a state of fusion at a sufficiently high temperature. In a state of fusion it acts energetically on the oxides, and if the metal will not unite with carbon—such as lead, tin, and bismuth—it is set at liberty, and can be separated or combined with other bodies, according to the condition of the experiment. If the metal or metalloid is capable of being carburised a double decomposition takes place, according to the formula—

$$RO + CaC_2 = RnC + CaO,$$

in which R represents the metal and n a variable number of atoms of carbon. By this method definite crystallised carbides of aluminium, manganese, chromium, molybdenum, silicon, &c., have been prepared.

Nomination.—M. Ditte was elected a member of the Chemical Section in succession to the late M. Schützenberger.

Influence of Altitude and Warmth on the Decomposition of Oxalic Acid by Sunlight.—M. and Mme. Vallot.—In a series of experiments, made simultaneously at Chamounix (altitude 1095 metres) and at Montanvert (altitude 1925 metres), considerably more decomposition took place at the higher station, the mean difference being 2·1 to 1 for a difference of level of 830 metres. Glass stops a large proportion of the chemical rays. The result of the experiments shows that temperature plays a more considerable part than would have been at first believed, but in the combined action of the two the greatest influence is exercised by light.

On the Alcoholic Isocyanurates, and the Constitutional Formula of Cyanuric Acid.—Paul Lemoult.—Not suitable for abstraction.

On Quinones and Hydroquinones.—Amand Valeur.—The author has studied the quinones and hydroquinones from the thermo-chemical point of view, and finds that the difference of the heats of formation of toluquinone and ordinary quinone is considerable (14·8 cals.), while that between benzene and toluene is only 6·4 cals. By neglecting the first terms of the two series, it is noticed that the homologous relations are parallel between the phenols and the quinones.

On the Absorption of Organic Matter by Roots.—Jules Laurent.—Grains of maize were sterilised by being kept in a weak solution of bichloride of mercury for two hours, and were then cultivated in a solution of, distilled water 1 litre, nitrate of lime 1 grm., chloride of potassium 0·25 grm., sulphate of magnesia 0·25 grm., mono-potassic phosphate 0·25 grm., and a few drops of a dilute solution of perchloride of iron: the maize developed normally, even to the complete opening of the flowers. On adding to the solution a known weight of glucose, and again of inverted sugar, it is found that the quantity of sugar absorbed is in *rapport* with the dry weight of the plant.

On the Analysis of Silicates.—A. Leclère.—This paper will be inserted in full.

Journal de Pharmacie et de Chimie,
Series 6, vol vi., No. 9.

Parisian Hospital Bread.—M. Balland.—Not suitable for abstraction.

On Retamine.—J. Battandier and Th. Malosse.—The molecular weight of retamine, determined by tonometry after being raised to boiling-point in solution in ethylic alcohol, has been found to be 269·4 and 268·3. The estimation of the carbon, hydrogen, and nitrogen has given C = 72·08, H = 10·69, N = 11·1, which corresponds almost to $C_{15}H_{26}N_2O$. Two bromhydrates have been prepared corresponding to $C_{15}H_{26}N_2O,HBr$ and $C_{15}H_{26}N_2O,2HBr$. Beautiful crystals of iodhydrate have been prepared, which appear to correspond to the formula $C_{15}H_{26}N_2O,2HI$. Sulphates corresponding to $C_{15}H_{26}N_2O,H_2SO_4(H_2O)x$, where $x=5$ for salts crystallised from aqueous solution, have been produced. Retamine combined with one equivalent of acid no longer colours phenolphthalein. The salts with two equivalents of acid, treated in aqueous solution with one equivalent of caustic alkali, are transformed into salts with one equivalent of acid, $R,2HBr + NaOH = R,HBr + NaBr + H_2O$. In this transformation, one molecule of soda corresponds with one molecule of retamine; the end of the reaction is indicated by phenolphthalein. Retamine will give neutral salts containing two molecules of a monobasic acid or one molecule of a dibasic acid for each molecule of the alkaloid; and basic salts containing one molecule of monobasic acid for one molecule of the alkaloid.

Researches on Urobiline and Biliary Pigments.—E. Lépinois.—As a rule, the detection of urobiline is a relatively simple matter, but if biliary pigments are present at the same time it becomes more difficult. The author has simplified the old method by adding a known quantity of chloride of zinc, then dilute ammonia—insufficient to dissolve the precipitate formed. It is then filtered, and the alkaline liquid, which has become limpid by filtration, is fluorescent if urobiline is present. Besides being fluorescent, the solution also gives a spectrum in which either normal urobiline (urochrome) or the abnormal urobiline of febrile urines can be detected.

Characteristic Reaction of Cotton-seed Oil.—G. Halphen.—The author finds that the red colour which he noticed some time ago when a sulpho-carbonic solution of the zinc salts of the fatty acids of cotton-seed oil was evaporated down to dryness is not due to the oxide of zinc at all, but that the sulphide of carbon alone will bring about the reaction, though only after a long time—so long in fact that it cannot be usefully applied to analysis. In trying to hasten the reaction, it was found that if both the oil and the sulphide were dissolved in amylic alcohol, the phenomenon was considerably accelerated. The best method of procedure is to mix in a test-tube equal parts of the oil to be tested, amylic alcohol, and sulphide of carbon containing 1 per cent of sulphur in solution. This tube is plunged into boiling salt water, so that one-half or two-thirds is above the surface; after ten minutes or a quarter of an hour the colouration appears if cotton-seed oil is present.

Commercial Preparation of Oxygen.—MM. Dutremblay and Lugan.—The authors hope to re-introduce, with improved apparatus and methods, the process used by Tessié du Motay in 1867, but since abandoned. It consisted of decomposing, by means of superheated steam at 500°, the alkaline manganates, which are re-generated at the same temperature by a dry current of purified air. The apparatus required is an air-pump, a purifier (to remove the CO_2 and H_2O), a furnace for the manganates, an automatic distributer (to introduce alternately air and steam into the retort), and a gas holder furnished with a refrigerator to condense the watery vapour drawn in. The reactions take place at a low pressure, and as the oxygen is carried into the gas holder by means of the steam instead of through a pump, it is kept perfectly free from carbides. The old disadvantages, which consisted in the caking of the charge and the evaporation of soda, have been rectified and done away with, and there is no longer now any danger of explosions occurring.

No. 10.

On Phosphoglycerate of Lime.—MM. Adrian and Trillat.—The method of preparing phosphoglycerate of lime now generally in use consists in heating a mixture of phosphoric acid and glycerine, for six consecutive days, to a temperature of 100° to 110°; the acidity is then neutralised with carbonate of lime and milk of lime, and the salt is finally precipitated with alcohol. Experiments have shown that the proportion of lime and phosphoric acid present is not constant, varying as much as from 19·5 to 24·5 for the former, and from 26·0 to 33·6 for the latter. Its solubility in distilled water at 25° varies from 4·05 per cent to 7·6 per cent. The residue left by the commercial substance after solution in water consists of sulphate and phosphate of lime, in proportions varying from 0·10 per cent to 7·5 per cent. A slight elevation of temperature in an aqueous solution suffices to precipitate phosphoglycerate of lime; the precipitation commences at 32°, is very abundant at 40°, and almost complete at 100°.

On the Reaction or Filter-paper.—L. Magnier de la Source.—The author finds that filter-paper always retains a small quantity of acid, no matter how thorough the washing with cold water may have been: it is for this reason that it acts as an acid in titrations of cream of tartar in boiling solution, as the boiling water extracts the last traces of hydrochloric acid.

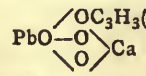
Qualitative Research on Traces of Alkaline Carbonates in presence of an Excess of Bicarbonates or of Borax.—Alex. Leys.—Already inserted in full.

On the Preparation of Distilled Waters.—M. Julliard.—The author does not agree with the report presented to the Pharmaceutical Society of Lyons by M. A. Lambert, on the revision of the Codex, that pharmacists are wrong in rejecting the preparation of aromatic waters by means of essences; his reason is, that in many cases distillation in itself causes an alteration of the molecular state of the essence.

On the Non-existence of an Intermediate Iodide of Mercury.—M. François.—Already inserted in full.

No. 11.

On Phosphoglycerate of Lime.—MM. Adrian and Trillat. — This paper is continued from the previous number. A sample of raw phosphoglycerate of lime gave on analysis 25 per cent of phosphoric acid and 22·5 of lime; after precipitation by heat, at a temperature of 70°, it gave 30 per cent of phosphoric acid and 23·25 per cent of lime. Contrary to the general opinion, phosphoglycerate of lime is not decomposed by prolonged heating at 100°. It has generally been described as an amorphous powder, but the authors have at last obtained it in the form of regular crystalline needles; when exposed to the air, however, these crystals gradually disintegrate, and form an amorphous powder. Purified phosphoglycerate of lime coresponds with the formula—



as given by Pelouze.

On the Origin of Artesian Water.—M. Lehache.—Not suitable for abstraction.

On Testing for Diastase from Barley.—P. Terrat.—The author shows that, in testing for barley diastase, the use of ordinary water is unsuitable, and may lead to the rejection of really good samples as being inferior: the chief cause of this difference in results is due to the alkalinity of the water, so small a quantity as 0·002 per cent of sodic hydrate reducing the titration of the diastase to 26 per cent of what it would be with a neutral water.

MISCELLANEOUS.

Australasian Association for the Advancement of Science.—The seventh meeting of this Association is now being held at Sydney, New South Wales, under the presidency of Prof. A. Liversidge, M.A., LL.D., F.R.S. The Association is divided into ten sections. Section B being devoted to Chemistry, under the presidency of T. C. Cloud, A.R.S.M., F.C.S., where papers will be read on "Metallurgical Methods in Use at Broken Hill," by G. H. Blakemore; "The Mineral Waters of Australasia," by G. Gray, F.C.S.; "Notes on the Constitution of Gluten," by F. B. Guthrie, F.C.S.; "The Characteristics of Australian and other Diamonds," by E. W. Streeter; &c. Besides these, there will be a large number of papers read in the other sections: those of "Ethnology and Anthropology" (Section F); and "Economic Science and Agriculture" (Section G), both having long and interesting programmes. The scientific side of the meeting will be agreeably leavened by entertainments and excursions; and we have no doubt but that this, the seventh meeting of the Association, will be as successful as the preceding ones.

McGill University, Montreal.—An additional Chair of Chemistry has been founded and endowed in this University by Mr. W. C. McDonald, who recently erected a new chemical building at a cost of 240,000 dollars. The same donor has provided an additional endowment of 50,000 dollars for the Faculty of Law, to the deanship of which Faculty, with the Chair of Roman Law, Mr. F. P. Walton, of the Scotch Bar, was recently appointed. Mr. McDonald has, moreover, supplemented the existing endowments associated with his name by a further gift of 200,000 dollars, to provide for any deficiency in income that may result from the fall in the rate of interest on investments.

On Silver Cyanamide, CN_2Ag_2.—Paul Lemoult.—Silver cyanamide is one of the most characteristic derivatives of cyanamide. It is formed by the reaction of an ammoniacal solution of NO_3Ag on an aqueous solution of cyanamide; it occurs as a yellow precipitate, but it is not easily obtained pure. To effect this, it must be suspended in water and acted on by an excess of HNO_3 in the cold. After filtration (the solution is never complete), the liquid is precipitated little by little with ammonia, and after repeating this severa times the pure product may be obtained.—*Comptes Rendus*, cxxv., No. 20.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 1990.

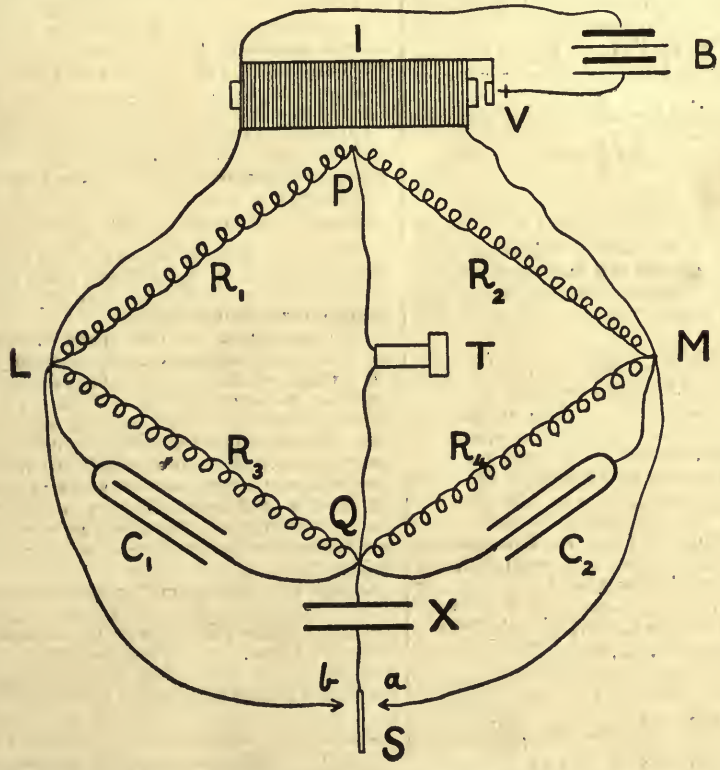
A NOTE ON

SOME FURTHER DETERMINATIONS OF THE DIELECTRIC CONSTANTS OF ORGANIC BODIES AND ELECTROLYTES AT VERY LOW TEMPERATURES.*

By JAMES DEWAR, M.A., LL.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution,
and
J. A. FLEMING, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London.

In several previous communications (see Fleming and Dewar, *Roy. Soc. Proc.*, 1897, vol. lxi., pp. 2, 299, 316, 358, 368, and 381) we have described the investigations made by us on the dielectric constants of various frozen organic bodies and electrolytes at very low temperatures. In these researches we employed a method for the measurement of the dielectric constant which consisted in charging and discharging a condenser, having the given body as dielectric, through a galvanometer 120 times in a second by means of a tuning-fork interrupter. During the past summer we have repeated some of these determinations, and used a different method of measurement and a rather higher frequency. In the experiments here described we have adopted Nernst's method for the measurement of dielectric constants, using for this purpose the apparatus as arranged by Dr. Nernst which belongs to the Davy-Faraday Laboratory. The frequency of alternation employed was 350 or thereabouts, whereas in all our formerly described experiments with the galvanometer method it was 120.

The electrical details of the arrangement employed in Nernst's method are as follows:—A Wheatstone's bridge is formed (see diagram), two sides of which consist of variable resistances, R_1, R_2, which are usually liquid resistances contained in U-tubes. The other two sides of the bridge consist of two sliding condensers of variable capacity, C_1, C_2, which are shunted by adjustable liquid resistances, R_3, R_4. The bridge circuit contains a telephone, T, as detector. The alternating currents are furnished by an induction coil, I. An experimental condenser, X, the dielectric of which can be made to be the substance under examination, is connected, as shown in the diagram, so that it can be placed in parallel with either of the shunted condensers forming the third and fourth arms of the bridge. The process of measurement is then as follows:—The experimental condenser is placed in parallel, by the switch S, say, with the third arm of the bridge, and the shunt resistances are first adjusted, so that the telephone gives a minimum of sound. The capacity of one sliding condenser, C_1, is then varied until complete silence in the telephone in the bridge is obtained. The experimental condenser is next shifted over into parallel with the fourth arm, and the capacity of the same sliding condenser is again adjusted to produce silence in the telephone. The change in capacity thus made in the sliding condenser corresponding to the change in position of the experimental condenser is denoted by *s*. The experimental condenser then has its air dielectric replaced by a liquid of known dielectric constant D_0, and the same process of change of its position effected. Let the variation of the adjustable sliding condenser then be denoted by S_0. Finally the experimental condenser has its air



* A Paper read before the Royal Society, December 9th, 1897.

dielectric replaced by a liquid or frozen liquid of unknown dielectric constant D, and the process of change and adjustment a third time repeated. Let the variation of the sliding condenser in this third case be S. It is then very easy to show that the following relation holds good between D_0, D, S_0 S, and s, viz.:—

$$\frac{D_0-1}{S_0-s}=\frac{D-1}{S-s}$$

or—

$$D=\frac{D_0-1}{S_0-s}(S-s)+1.$$

In order to apply this method we employed absolute ethylic alcohol as the standard dielectric substance of known dielectric constant, and took as its dielectric constant at 15° C. the value 25·8 (according to Nernst), a number closely in agreement with all the best results by other observers.

The actual capacity of the experimental condenser with air as dielectric was very small, not being more than about 0·00001 of a microfarad. Hence in the above formula $D_0=25·8$.

The value of s was determined to be 1·33 and 1·38 in two experiments, and the mean 1·36 was taken as the value of s.

The following liquids were then examined by placing them in the experimental condenser and keeping them at ordinary temperatures, viz., 16° C. to 20° C.

1. Solution of potassic hydrate in water, 5 per cent solution.
2. Solution of rubidic hydrate in water, 5 per cent solution.
3. Amyl alcohol.
4. Ethylic ether.
5. Ethylic ether, pure and dry.
6. Ethylic alcohol.

The change in capacity of the sliding condenser when ethylic alcohol replaced the air in the experimental condenser was 16·7. Hence $S_0=16·7$ and $D_0=25·8$, also $s=1·36$.

Therefore—

$$\frac{D_0-1}{S_0-s}=\frac{24·8}{15·34}=1·613.$$

The following table shows the observed values of s in the several cases when the above liquids were placed in the experimental condenser, and the corresponding calculated value of the dielectric constant D, where—

$$D=1·613\times(S-s)+1.$$

Table I.—*Determinations of the Dielectric Constants of certain Liquids at Ordinary Temperatures* (15° C.) *by Nernst's Method. Frequency* = 320.

Substance.	S.	S−s.	1·613 (S−s).	Dielectric constant =D.
Ethylic alcohol (taken as the standard of comparison)	16·7	15·34	24·8	25·8 (assumed value)
Amyl alcohol	10·49	9·13	14·7	15·7 (calculated)
Ethylic ether	3·98	2·62	4·23	5·23 (calculated)
Pure dry ethylic ether	3·70	2·34	3·78	4·78 (calculated)

Hence by Nernst's method, assuming the dielectric constant of ethylic alcohol to be 25·8, we find that of amyl alcohol to be 15·7 and pure ethylic ether to be 4·78.

Nernst himself found amyl alcohol to be 16·0 and ethylic ether to be 4·25 at about this temperature. Hence our values are in fair agreement with his.

In the next place we cooled the experimental condenser down to the temperature −185° C. in liquid air, after filling it with one of the above six dielectric liquids, and we repeated all the above-described operations again. The results are collected in Table II.

Table II.—*Determinations of the Dielectric Constants of certain Frozen Liquids at the Temperature of Liquid Air by Nernst's Method. Frequency* = 320.

Substance.	S.	S−s.	1·613×(S−s).	Calculated dielectric constant =D.
Ethylic alcohol	2·68	1·32	2·13	3·13
Amyl alcohol	2·34	0·98	1·58	2·58
Ethylic ether	2·16	0·80	1·29	2·29
5 per cent solution of rubidic hydrate ..	2·94	1·58	2·55	3·55
5 per cent solution of potassic hydrate ..	5·15	3·79	6·12	7·12

The above values for the organic bodies are in close agreement with the results we obtained for the same substances by the galvanometer and switch method formerly used by us, as may be seen by a reference to Table III.

Table III.—*Comparison of the Determinations of certain Dielectric Constants made by Different Methods at the Temperature of Liquid Air.*

Substance.	By galvanometer and switch method. Frequency = 120. Dielectric constant.	By Nernst's bridge method with telephone. Frequency = 320. Dielectric constant.
Ethylic alcohol ..	3·11	3·13
Amyl alcohol ..	2·14	2·58
Ethylic ether ..	2·31	2·29
5 per cent solution (aqueous) of potassic hydrate ..	123·0	7·12
5 per cent solution (aqueous) of rubidic hydrate ..	81·6	3·55

The results collected in the above Table III. show that the two methods give practically identical values for the two alcohols and the ether, but very different value for the two frozen dilute hydrates.

An examination was then made of several other substances, and for this purpose another condenser was constructed, which consisted of a platinum crucible about 4 c.m. in diameter and 5 c.m. high. This crucible was fitted with an ebonite lid, through which passed a glass test-tube, in the interior of which was placed our platinum thermometer. Round the outside of the test-tube, platinum wire was closely wound, so as to form the opposed surface of a condenser in relation to the platinum crucible as the other surface. This platinum condenser could then be filled with any electrolyte or organic liquid and frozen in liquid air.

Owing to the very small actual capacity of this last experimental condenser, and especially that of the variable part of it in comparison with the capacity of the leads and connections, no very great accuracy of measurement was looked for or attained. The results, however, were sufficient to check the general accuracy of the experiment with similar substances by the galvanometer method. This platinnm condenser was calibrated and used with the Nernst bridge, exactly as in the previous experiment.

With the experimental condenser empty, the change in capacity of the variable sliding condenser in the bridge arm was 1·50 on changing over the position of the experimental condenser. Hence $s=1·50$.

When filled with ethylic alcohol ($D_0=25·8$) the change of capacity of the sliding condenser was 6·20. We have, therefore, $S_0=6·20$, $D_0=25·8$, $s=1·50$.

Therefore—

$$\frac{D_0-1}{S_0-s}=\frac{24·8}{4·70}=5·27.$$

The experimental condenser was then filled with some liquid, either at ordinary temperature or frozen at a low temperature, and the bridge measurement made, and the reading S or the change of capacity of the sliding con-

denser observed, as before, when the experimental condenser had its position changed.

The following Table IV. gives the summary of the results obtained with several substances at various temperatnres.

TABLE IV.—*Measurement of the Dielectric Constants of various Substances at Different Temperatures by Nernst's Method. Frequency* = 350.

$$S = 1{\cdot}50, \frac{D_0 - 1}{S_0 - s} = 5{\cdot}27.$$

Substance.	S.	S−s.	5·27 (S−s).	Calculated dielectric constant =D.	Temperature in platinum degrees.
Ethylic ether	2·1	0·6	3·16	4·16	+15°
Glycerin ..	12·15	10·65	56·2	57·2	+30
Solution of ammonia (sp. gr. = 0·880) ..	4·5	3·0	15·8	16·8	−123 (?)
	5·6	4·1	21·6	22·6	−137
	13·5	12·0	63·0	64·0	−119
Distilled water or pure ice	0·2	0·5	2·6	3·6	−49
	11·0	9·5	50·0	51·0	−7
	14·3	12·8	67·0	68·0	+1
Oxide of copper in suspension in water	3·95	2·45	12·9	13·9	−61
	12·8	11·3	59·7	60·7	−41

The value found for the dielectric constant of water at +1° is rather low, but, as above mentioned, the smallness of the capacity of the experimental condenser prevented the results from being more than good indications of the *order* of the dielectric constant.

(To be continued).

THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.

By Professor W. W. ANDREWS.

In a paper published last October in the *Journal of the American Chemical Society*, entitled "Some Extensions of the Plaster of Paris Method in Plowpipe Analysis," the author gave some account of the development of this method since Dr. Eugene Haanel first proposed this new support. The new composition of the tablets, the new easily prepared and portable reagents, and the reactions they yield with the metals were there described. The author now gives some new applications of this support and some new reactions. The iodide coatings of the metals are shown.

The addition of boric acid to the calcium sulphate in the manufacture of the tablets so fortifies them that they form a substitute, not only for charcoal, but also for platinum wire and bone ash. They resist the action of the fluxes of borax and metaphosphoric acid, and instead of beads in platinum loops we may with advantage produce coloured glassy films on the surface of the white tablets. Oxidation and reduction take place very readily in these films. All degrees of saturation may be observed at once. The colour changes due to change of temperature may be more accurately observed on account of the slower rate of cooling.

In assay work, if a fragment of a tablet be heated to redness for a few seconds andthen pulverised, we have a material which may be moulded into a smooth cupel which does not blister, and which very readily absorbs the lead oxide in cupellation.

Potassium sulphocyanate, metallic iodine, potassium cyanide, potassium sulphide, and potassium-cadmium cyanide are all easy to carry. With water they easily dissolve, and therefore solutions may be prepared anywhere. In the laboratory more rapid and better work can be done with the solutions. Potsssium sulphocyanate is not always kept by the druggists, and its preparation by crystallisation in the laboratory is tedious. The simplest way to prepare the iodine solution is to mix fragments of potassium cyanide and sulphur, the latter a little in excess of the molecular proportions, in a test-tube and fuse together, adding water while yet warm, and then adding metallic iodine to saturation. Dr. Wirt Tassin, of Washington, uses a solid reagent made by fusing iodine and the sulphocyanate together with a little sulphur, and then powdering. This, if stable, ought to prove very satisfactory.

Here is a very effective portable blowpipe lamp which cost less than two cents. It consists of an ordinary druggist's tin salve box, with a piece of tin bent to form a wick-holder. The cover is bulged so as to shut down over the wick. The fuel is paraffin wax or stearin. The flame is smokeless, very hot, and with great reducing power and free from sulphur. Once filled it burns for more than an hour. A test tube can be readily boiled over it. In private laboratories, and in schools in towns, where the electric light has supplanted gas, and afield this little piece of simple apparatus should prove useful.

Some reactions, not hitherto published, are those obtained by using the tablets as infusible filters. Films are obtained, for which I propose the name "solution films," to distinguish them from the sublimation films.

If to a solution of a lead salt a little potassium sulphocyanate and iodine be added, a precipitate of lead iodide tends to form. When, however, no precipitate is visible, if a drop be let fall on a tablet instantly, a bright-yellow spot is seen. The delicacy of many tests may be greatly increased by making use of this property of the tablets. It seems to be somewhat catalytic. Not only one, but as many as fifty or one hundred drops may fall upon the same spot, each drop deepening the colouration.

The iodine solution shows a remarkable power of dissolving gold. Gold leaf dropped on its surface almost instantly dissolves. If the solution containing gold be dropped on a tablet and the spot touched with the blowpipe flame, a fine pink film appears. One drop of solution containing one part gold in thirty thousand will show a fine pink. Fifty drops will show gold present in one part in six hundred thousand, and one hundred drops one part in one million of solution. The test, therefore, may be made quantitative.

Platinum yields a slate-coloured film, chromium a film dark-green hot, and fine green cold. Copper yields a purple film, which, treated with sulphuric acid, disappears and darkens in oxidising flame. If a copper solution be dropped on a tablet and heated vapours of hydrobromic acid be blown over it, the purplish brown of cupric bromide will appear. This will reveal copper, when present, one part in two million parts of solution.

Iron gives a brownish film, which sulphuric acid turns to Venetian red, and other acids remove. A little metaphosphoric acid added to the solution will prevent the formation of the film. Cobalt yields a pink film, which becomes, on hydration, a beautiful blue, and more strongly heated a black, which a drop of strong acid potassium sulphate removes.

Nickel yields a pale green film, which, dehydrated, becomes a brownish yellow and then a black. Ammonium hydrate turns the solution a fine blue.

Nickel may be detected in the presence of cobalt. The solution will probably be colourless, unless iron be present, when it will be amethystine. If a drop of the iodine solution be added to the section of the tablet wetted by the metallic solution, and heated, the centre will be black, showing nickel, for in such circumstances the cobalt tends to leave a white centre, forming a black ring with sometimes a blue ring separating it from the centre, outside that a brownish yellow showing nickel, and further out a spreading blue showing cobalt. The

* Read before the British Association (Section B), Toronto Meeting, 1897.

salts experimented with were the nitrates and sulphates, and when cobalt was six times as abundant as the nickel, the reactions of the latter were well marked.

Manganese, vanadium, molybdenum, ruthenium, and osmium also yield solution films.

Potassium-cadmium cyanide has been found to be a reagent which affords a very delicate and ready test for sulphur even in the presence of selenium and tellurium.

Potassium sulphocyanate solution was added to a cadmium solution and dropped on a tablet and heated, and the scarlet of hot cadmium sulphide showed itself. Sixteen drops revealed the presence of cadmium in a $\frac{1}{100}$ normal solution, and this test was not interfered with by the presence of two hundred times as much zinc.

Zinc in the cobalt test responded with great delicacy, but aluminium gave no satisfactory results.

Another extension of this method is to the compounds of organic chemistry.

Carbon gives a sooty coating which metaphosphoric and sulphuric acids increase. Tars and asphalts give a black tinged with green.

The phenols with the same reagents yield a black edged with a pinkish red. Picric acid is the only exception found so far. It gives a yellow. The following were among the phenols treated—carbolic acid, pyrogallol, salicylic acid, oils of coniine and wintergreen, Canada balsam, Burgundy pitch, resin, phenolphthalein, hydroquinone, and creolin. Many of the phenols when dropped on a tablet previously heated before the blowpipe show very brilliant and characterestic colours.

The paraffins yield no red, but heavy sooty, films.

HYSTERICAL CHEMISTRY.*

By Prof. H. CARRINGTON BOLTON, Ph.D.

(Concluded from p. 5).

Gustav Marqfoy is a writer on chemistry less fanciful than those cited, yet worthy of a place among hysterical chemists. In his "Loi des Equivalents et Théorie Nouvelle de la Chimie" (Paris, 1897) he admits the unity of matter, and reduces the number of undecomposable bodies to 63. The equivalents of these 63 simple bodies are prime numbers, forming a natural series from 1 to 300. The atom he regards as made of a nucleus and a plasma; the nucleus is the seat of energy. His view of the successive steps in the creation of the elements, in accordance with the arithmetical chain he discovered, is interesting, but not easily abstracted.

In this group of esoteric students the most picturesque personage is August Strindberg — a Swede by birth, a Frenchman by adoption, an Austrian by residence (temporary perhaps)—he is thus portrayed by one of his admirers:—Pale blue, dreamy, sympathetic eyes; a broad forehead, on which the fire of genius burns with brilliancy; slow of speech, with a marked Scandinavian accent, he attacks boldly the "routine and persecuting scientists;" a "superb man," disinterested, mild, invincible in perseverance, and seeking only the truth. Strindberg is a man of letters, being the author of successful romances and dramas,† and he claims to be a chemist, but his right to this claim can be better determined after analysing his pretensions.

Strindberg accepts the theories of the unity of matter, the self-evolution of elementary bodies, the transmutability of elements, and hylozoism; he even grants to matter the principles of heredity, memory, and love. His strength, however, lies in his peculiar method of demonstrating that the chemical elements are compounds, and in discovering new formulæ for well-known substances. More proficient in manipulation than his Monist friends, he invokes results of laboratory work to confirm his demonstrations. With admirable courage he attacks problems in chemistry of herculean difficulty, and does not hesitate to undertake to disprove orthodox views of most fundamental facts, such as the composition of the atmosphere, the composition of water, and all the important phenomena depending thereon. Exhibiting considerable knowledge of the literature of chemistry, he is quick to discern in the earlier writings statements that he can turn to his advantage, ignoring the circumstance that the very statement on which he relies has often been shown to be erroneous by later authorites. He writes, for example, "Lampadius believed that carbon disulphide was composed of sulphur and hydrogen, had he said carbon and hydrogen I would bless his memory." Avicenna, Albertus Magnus, Paracelsus, Bœrhaave, Berzelius, Bunsen, and Clève are, for Strindberg, authorities of equal weight. He uses on one page the very arguments which on another page he condemns when employed by "official" chemists, and he claims that the latter suppress the dogmas of hysterical chemistry to avoid the unpleasant necessity of revising theories of scientific chemistry. "About sixty years ago," he writes, "a French chemist decomposed chlorine and obtained 3 per cent of oxygen, but his discovery was buried to save appearances" (*Hortus Merlini*).

Strindberg denies the idea of an undecomposable body. "Is there truly a chemist," he asks, "who believes that iron dissolved in sulphuric acid is not decomposed?" He uses current chemical terms with changed meanings: precipitation signifies reconstruction; solution signifies decomposition; and combustion, synthesis—an original nomenclature that obscures his writings.

> "The atom is an hypothesis,
> An hypothesis has no weight, therefore
> Atomic weight is a non-entity."

In spite of this remarkable syllogism, with which Strindberg opens one of his essays, he makes most of his discoveries (?) by juggling with the numbers representing these very atomic weights. When the molecular weight of a compound happens to be equal to the atomic weight of an element, or to the molecular weight of some other compound, he assumes that this accidental correspondence involves close relationship—if not identity—of substance, and he audaciously substitutes one formula for the other. In his "Introduction à une Chimie Unitaire" (Paris, 1895), Strindberg opens the topic with the motto "*Omnia in omnibus, omne omne est*," and proceeds thus:—"Bodies exist only in numbers and qualities; bodies are neither simple nor compound. Chemical formulæ are merely methods of expressing the manner in which bodies differ and correspond."

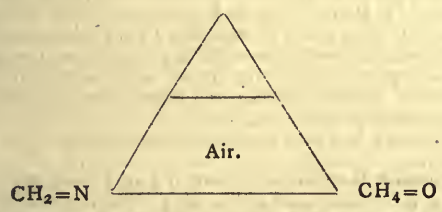
"That which is called hydrogen is neither a simple body nor a compound body; it is matter having the condensation 1. Carbon can be formulated thus: $H_{12}=C$; oxygen in the same way, H_{16} or $CH_4=16=O$; nitrogen likewise, H_{14} or $CH_2=14=N$; though nitrogen in combination may have the formula $N_2=28$." To the molecule of nitrogen he assigns the formula CO, because its molecular weight is 28. His method of reasoning is as peculiar as his choice of formulæ:—"By assigning to nitrogen the formula CH_2 or C_2H_4, and to carbonic acid the formula N_2O, a whole series of phenomena hitherto obscure are explained. Thus the *rôle* of nitrogen in animal and vegetable economy: the nutrition of animals by carbohydrates, and the great excess of nitrogenous matter secreted; the miraculous way in which plants nourished with water and air produce carbon and albumenoids without absorption of nitrogen and without sufficient carbonic acid, the latter being only an impurity of the atmosphere (4 parts of CO_2 in 10,000 of air); the transformation of starch into albumenoids; and,

* Read to the Washington Section of the American Chemical Society, November 11th, 1897.

† His "Sensations d'un Détraqué" was published in *Figaro*. His drama "Magda" was acted at the Renaissance, Paris, by Sarah Bernhardt.

lastly, the origin of the creation by water and air, even Pasteurised, at the beginning of time." According to this ingenious philosopher, "that which is called air is neither a mixture nor a combination; it is neither oxygen nor nitrogen; it is both or neither. Since the atomic weight of carbon varies from 11 to 12 (?), nitrogen may be indicated by CH_2 or CH_3; since oxygen varies from 15 to 16, it may be represented by CH_3 or CH_4; therefore, in the conditions in which oxygen appears identical with nitrogen, both are represented by CH_3. Air is therefore CH_3, which signifies oxygen and nitrogen." Having thus established a novel formula for air, he proceeds to discuss on that basis its function in combustion, oxidation, and respiration: reverting to the alchemical symbol for air, $\underline{\Delta}$, he gives the following lucid diagram, which summarises the knowledge of hysterical chemists concerning the atmosphere:—

$$N{=}CH_3{=}O$$



Strindberg takes up the chief elementary bodies and treats them in like manner; to chlorine he gives the formula $(OH_2)_2$ or $2H_2O$, and this, he says, explains the presence of chlorine in sea-water. With other well-known compounds he is equally successful:—

$$SO_3H = CH_5O_4 = CH_4O_3(OH)$$
$$HCl = (H_2O)_2 = H_3O(OH) = COH_7.$$

And by applying his method to metals he secures some startling results:—

Iron	$= (C_2H_4)_2$	= 56	
Manganese	$= (C_2H_3)_2$	= 55	
Zinc	$= (CH_4O)_2$	= 64	
Copper	$= (CH_4O)_2$	= 63	
Copper	$= C_2H_5Cl$	= 63	
Silver	$= C_2H_5Br$	=107	
Gold	$= Fe_2Si_3$	=197	[196]
Gold	$= Fe_3S$	=197	[200]
Sodium	$= C_2$	= 24 (23)	
Calcium	$= C_3H_4$	= 40	
Nickel	$= C_2H_5P$	= 58	
Cobalt	$= C_2H_5S$	= 59	

Of the two latter formulæ Strindberg remarks:—"Cobalt and nickel have always been suspected to be compounds, and I believe I have solved the problem of their enigmatical atomic weights."

The fact that the above equations are not always true, that many of the arithmetical calculations are inaccurate, that a few of the substances formulated are purely imaginary, and that the atomic weights occasionally differ by a whole number from the standard, does not at all disturb the equanimity of this Monist philosopher; when discrepancies of any kind are pointed out to him, he simply responds:—"Chemists always find impurities in the flasks of others, and never in their own."

"*Similia similibus dissolventur; similia similia appetunt*" is another maxim that this author illustrates as follows:—Copper dissolves best in concentrated nitric acid because they have the same weights:—

$$Cu = 63 = HNO_4.$$

Gold dissolves in aqua regia:—

$$Au = 197 = 2HCl + 2NO_3.$$

Zinc dissolves best in sulphuric acid:—

$$Zn = 65 = (CH_4O)_2.$$

But $CH_4O = S$, and

Sulphuric acid diluted $= SO_4 + 2H_2O = 65 \times 2$.

The chlorides in general are soluble in water, because of the constitution of chlorine, which is $(OH)_2$ or O_2H_2

In his "Hortus Merlini" (first letter) Strindberg undertakes to demonstrate the compound nature of sulphur, claiming for it a constitution analogous to a fossil resin. After a detailed study of its external properties and its physical changes when heated, he recounts some original experiments, such as reduction of melted sulphur by the green twig of a chestnut tree (!), and burning sulphur in carbonic acid, which, he says, yields a deposit smelling like pepper; he claims that spectroscopic analysis of hydrogen flame shows the spectrum of sulphur; these and a score of equally convincing data go to prove that sulphur is a compound of C, H, and O. He ingeniously concludes thus:—"To require me to give a definite formula for sulphur would be indiscreet." Elsewhere he writes of "selenium the parent of sulphur."

Perhaps the best example of Strindberg's peculiar line of reasoning is found in an article entitled "La Synthèse de l'Iode," published in *L'Hyper-Chimie* for January, 1897:—"Sea-water contains not a trace of iodine, and consequently the algæ must produce it by synthesis. But living algæ yield no iodine, and do not yet contain it. The ashes of algæ, however, furnish iodine through the intervention of reagents; so it is evident that iodine is formed by a commutation of the crude materials in algæ and reagents. The old method of extracting iodine was by treating the mother-liquors with sulphuric acid and manganese dioxide; wherefore manganese? Because there exists an occult correspondence between the algæ, iodine, and manganese, which manifests itself in the colours they yield. Algæ occur of brown, greenish blue, reddish purple, and violet colours, and these same colours appear in iodine and in compounds of manganese." Strindberg then points out that there is a constant difference of 46 between the atomic weights of Cl, Br, and I; and having previously demonstrated that the correct formula for Cl is $(OH)_2$, he then seeks for the body which has the weight 46. Finding a choice of three substances, viz.,—

Ethyl alcohol	$= C_2H_6O$	= 46
Formic acid	$= CH_2O_2$	= 46
Nitrogen peroxide	$= NO_2$	= 46,

he selects formic acid, because the starch in the algæ is changed to sugar by sulphuric acid, and this sugar oxidised by manganese dioxide yields formic acid, so that he gets the following formula for iodine:—

$$I = 126 = (CH_2O_2)_2(OH)_2.$$

Later in this amazing essay he regards iodine as a derivative of benzene,—

$$\text{Oxyhydroquinone} = C_6H_6O_3 = 126 = I;$$

as experimental proof of this correspondence he states that oxyhydroquinone heated with alcohol gives out a vapour that colours starch test-paper blue and colours bread yellow, just as iodine does.

He offers to manufacturers of iodine practical suggestions based on these vagaries, which are too absurd to transcribe.

Denying the elementary character of the metals, Strindberg naturally believes in transmutation, and claims to have accomplished the "great work" in more than one instance. By dissolving pure copper in linseed oil, he finds in the product by analytical tests only nickel, and he claims to have obtained gold from lead and sulphur. He appeals to the transforming power of growing plants as proof of transmutation in Nature, and he ridicules the methods of official analytical chemists who examine the *ashes* of plants to ascertain the nature of the plants:—"Does anyone make an inventory of the treasures of a palace by setting fire to the four corners of a Raphael or a Rembrandt, and does he determine their value by the remaining traces of cinnabar, white lead, and chrome yellow?"

This convincing method of reasoning he employs in another connection:—"People ask me if I can make gold, and I reply, 'To draw the genealogical chart of the ancestors of a cat, I do not need to know how to make a cat!'"

Though their theories and methods are indisputably original, hysterical chemists, so far as appears from their writings, have contributed nothing whatever to advance the science they profess to admire. If anyone of their number appears to be a genius, it must be remembered that "a genius is a man who is almost a fool." Moreover, paraphrasing Rabelais,—

"The world of fools hath such a store
That he who would not see an ass
Must bide at home, bolt his door,
And break his looking-glass!"

CONTRIBUTION TO THE STUDY OF THE NITRIFICATION OF SOILS.

By TH. SCHLŒSING, Jun.

NITRIFICATION, and the microbial combustions of organic matters generally, are, as a rule, more active in rich soils than in light ones. This is a recognised fact, concerning which M. Muntz has given definite examples, and with which practical men agree, by saying that strong soils conserve manure. It is generally explained by the greater facility with which the air penetrates light soils.

In most cases, however, it is not the air—I do not say in all cases (see the work of M. Dehérain on this subject, *Comptes Rendus*, vol. cxxi.)—but the absence in strong soils of the water which is necessary for the complete combustion to go on.

Normally, when water is not present in excessive quantities, it does not fill up the interstices between the solid particles, but is spread over the surface of these particles in thin layers, which form a uniform covering as a whole. For an equal proportion of moisture in an earth, the thickness of these layers diminishes as the fineness of the particles increases, because of the increasing total surface of the latter. In a soil containing 10 per cent of water and a good proportion of clay (a substance composed of particles in a very fine state of division) this fineness may become so extreme as to seriously interfere with the nourishment of the microbes.

I now give a few experiments relating to the nitrification of ammonia, in which I have endeavoured to determine the influence of the thickness of the layers of water with which the particles of the soil are coated. I have made artificial soils from the following ingredients, in which the mixture was made as homogeneous as possible:—Quartz sand, from Bonnevault, in which the grains had an average diameter of ⅛ m.m.; clay, from Vauves, the particles of which had an average diameter of 1 μ; chalk, from Meudon; and water holding in solution a known quantity of sulphate of ammonia, and of which a part had been shaken up with a little earth, so as to be charged with nitrifying microbes, and then decanted. The mixtures were placed in separate flasks, large enough for there always to be an abundant supply of oxygen, and kept from such variations of temperature as would cause loss of moisture by evaporation. The nitric acid formed was eventually estimated.

Each lot, at the commencement, contained 50 m.grms. of sulphate of ammonia = 40·9 m.grms. N_2O_5.

FIRST SERIES.—*January 14 to March 27. Temp. 26—27°.*

Composition of the soils.	I. Grms.	II. Grms.	III. Grms.	IV. Grms.	V. Grms.
Sand	100	90	80	75	70
Clay	0	10	20	25	30
Chalk	0·5	0·5	0·5	0·5	0·5
Water	10	10	10	10	10
N_2O_5 found (m.grms.)	34·1	38·5	36·2	23·5	4·23
N nitrified (per cent)	83	94	89	56	10

The same experiments were repeated, but the solid particles were first of all sterilised, and, as a check, the unnitrified ammonia was also estimated.

Each lot, at the commencement, contained 100 m.grms. of sulphate of ammonia = 81·8 m.grms. N_2O_5.

SECOND SERIES.—*July 17 to November 1. At the Temperature of the Laboratory.*

Composition of the soils.	VI. Grms.	VII. Grms.	VIII. Grms.	IX. Grms.	X. Grms.	XI. Grms.
Sand	100	90	85	80	75	70
Clay	0	10	15	20	25	30
Chalk	1	1	1	1	1	1
Water	9·5	9·5	9·5	9·5	9·5	9·5
N_2O_5 found (m.grms.)	51·2	54·1	77·1	81·9	17	2·2
N nitrified (per cent) .	63	66	94	100	21	2·7

The results of these two series are in accord. Complete, or almost complete, nitrification takes place in numbers II., III., VIII., and IX; decidedly weaker nitrification takes place in numbers IV., V., X., and XI. In other words, those containing 25 per cent or more of clay, and representing relatively strong soils, have undergone but little nitrification, while those corresponding to light soils have nitrified very well.

In numbers I. and VI. the nitrification was very incomplete, and the presence of nitrous acid was detected. It is probable that the proportion 9·5 or 10 per cent of water in pure sand was too much; the water evidently occupied too much of the interstitial spaces, and thus the aëration was insufficient.

If the nitrification was interfered with in numbers IV., V., X., and XI., can it be attributed to a want of air throughout the soils? No; and for this reason: that the soils, by the very method of their preparation, were thoroughly disintegrated, and in no way caked, but quite permeable; anyone who saw them could never believe that the aëration was insufficient. But the best answer to the question may be found through the following experiments, in which only the proportion of water was varied.

At the commencement, each lot contained 66·6 m.grms. of sulphate of ammonia = 54·5 m.grms. N_2O_5.

THIRD SERIES.—*April 1 to June 12. Temperature 26°*

Composition of the soils. Solid matters sterilised.	XII. Grms.	XIII. Grms.	XIV. Grms.	XV. Grms.
Sand	70	70	70	70
Clay	30	30	30	30
Chalk	0·5	0·5	0·5	0·5
Water	10·6	11·5	13·2	14
N_2O_5 found (m.grms.)	43·6	55·9	53·9	53·2
N nitrified (per cent)	80	100	100	100

We see here that by slightly increasing the amount of water—from 9·5 to 11·5 per cent—we have made the nitrification of the ammonia complete, where it was only partial. Now, this addition of water has rather diminished than increased the aëration, the liquid added occupying a part of the interstitial spaces formerly empty. It was therefore water, and not air, that was wanting in the soils containing 25 per cent and more of clay.

The strong soils of fields are often in this condition, that, though not wanting more air, they are short of water, so that nitrification and other microbial combustions are very much retarded; and it is for this reason that organic matters are consumed less quickly than in sands and coarser soils, where less water suffices.

Now, how is it that the want of water acts on the microbial combustions in soils? Let it be noticed that in the experiments quoted above (first and second series) its effect was distinctly shown in passing from soils containing 20 per cent of clay to those containing 25 per cent, and inversely that it was sufficient to add to the

soils very little water (third series) for its effect to be counteracted.

Between these two classes of soil—one nitrifying exceedingly well, the other badly—we can see no difference except in the thickness of the layers of water covering the particles; but even this difference was not great—in the one case 0·15 μ, and in the other case 0·13 μ (according to a rough calculation made with the object of getting some idea of the amount of difference). Thus, by increasing the proportion of clay only very slightly—that is to say, by diminishing the thickness of the layer of water by very little, we have considerably reduced the working capacity of the microbes, and we have restored this power by increasing the thickness again by even a very small amount. May we not therefore presume that, in diminishing this thickness beyond a certain point, we have reached a limit beyond which capillary attraction acts on the water and the dissolved principles with more force than the osmose, which causes the waters and the matters in solution to penetrate the microbial cells? The microbes have thus become unable to draw their nourishment from the soil. In any case it is interesting to see that so slight a variation in the thickness of the layer of water can have such a retarding action on the work of the microbes.—*Comptes Rendus*, cxxv., No. 21.

ON A NEW METHOD FOR THE ATTACK OF PLATINUM.

THE PREPARATION OF BROMO-PLATINATES OF AMMONIUM AND OF POTASSIUM.

By GEORGE MÉKER.

Platinum is considered to be unattackable to a large extent, while some saline mixtures which are looked upon as inactive attack it with great readiness.

Platinum, even when in a very fine state of division, resists the action of melted sulphate of ammonium; the alkaline chlorides and bromides affect it only to an inconsiderable degree at temperatures between 250° and 350°; but, on the contrary, in the event of using a mixture of these salts, and above all with sulphate and bromide of ammonium, or what comes to the same thing, sulphate of ammonium and bromide of potassium the corrosion of the metal is very rapid.

If we heat such a mixture in an ordinary platinum crucible for some few instants, we can see that the surface where contact takes place becomes bright red, while the metal undergoes a corrosion similar to the well-known appearance of etched iron.

I have proved that the red salt thus formed is bromoplatinate of ammonium.

The only mention of the preparation of this salt up to the present time has been by Topsoë in 1868. This preparation consisted in the combination of bromide of ammonium with the tetrabromide of platinum. The latter salt was difficult to obtain, and I have endeavoured to use the method of the direct attack of platinum for the purpose of obtaining the bromoplatinate of ammonium with as little trouble as possible.

For this purpose we slowly melt in a porcelain crucible six parts of ordinary sulphate of ammonium, then, when the salt is melted and the temperature at about 300°, we add, while stirring, one part of bromide of ammonium, or for greater simplicity powdered bromide of potassium with which has been incorporated, by grinding together, platinum black, or even finely divided metallic platinum.

We must keep the whole stirring at about 330°, and it will quickly become bright red, and froth considerably, while at the same time white vapours of bromide and sulphide of ammonium will be given off. After heating for ten or fifteen minutes the mass is poured out and dissolved in the smallest possible quantity of water and filtered. On the filter there remains a vermillion-red precipitate, while the solution will not contain any sensible amount of platinum; the salt formed being either insoluble or almost insoluble in ammoniacal salts. The precipitate is washed with a little cold water until the latter begins to be slightly coloured; the receptacle is then changed, and the filter washed with boiling water. The bromoplatinate goes into solution, and there remains a slight residue of undissolved platinum. The aqueous solution of the bromoplatinate, on being concentrated and cooled, deposits crystals of a bright crimson-red colour of great brilliancy, soluble in about two hundred times their weight of water.

The analysis of these crystals shows that they consist of pure bromoplatinate of ammonium.

	I.	II.	Theory per cent.	Found per cent. Average.
Substance ..	0·346	0·242	—	—
Platinum (by calcination)	0·095	0·0665	27·32	27·24
Substance ..	0·348	0·4425	—	—
Platinum (by magnesium)	0·097	0·123	27·32	27·68
Bromine ..	—	—	67·60	66·96
Nitrogen ..	—	—	3·94	3·85

The estimation of the platinum was carried out by two different methods; by direct calcination, and by precipitation by means of magnesium. In the latter case the figures obtained were always a trifle high, because of the traces of impurities contained in the magnesium. The bromine was estimated in the mother-liquors, from the precipitation of the platinum in the state of bromide of silver.

As in the case of the chloroplatinate, potash does not displace all the ammonium from the bromoplatinate; it is only by precipitating the platinum by magnesium that the magnesia formed by the action of the boiling water completely liberates the ammonia and makes the estimation possible.

By the method which has just been described, bromoplatinate of ammonium can be prepared in abundance with the greatest ease; but at the same time it must be borne in mind that, under the same conditions in other respects, the platinum is transformed only in proportion to the state of fineness in which it exists. In the state of sponge, or of very fine platinum black which has not been rendered metallic by rubbing, about two-thirds of the metal can be converted into the salt; the remainder, enveloped in a coating of crystals of bromoplatinate insoluble in the liquid, is not attacked. When using thin plates or filings it is advisable to rub the bottom and sides of the bath of the molten material so as to keep presenting new surfaces for the reaction. It is worthy of remark that the crystals of bromoplatinate deposited from a warm solution on cooling, take the form of cubo-octahedra, on which the octahedric facets are well developed, while those deposited by the spontaneous evaporation of a cold solution much more nearly resemble the cube.

By evaporation in the open air, we obtain, after a few months, cubical crystals of 2 m.m. to 2·5 m.m. in length, and occasionally possessing slight octahedric modifications. If we attempt to replace the bromide of ammonium or potassium by the chloride, we do not obtain a definite reaction; there is certainly a small quantity of chloroplatinate of ammonium formed, but there are at the same time ammoniacal derivatives, formed by the action of the products of decomposition of the sulphate of ammonium on the choroplatinate, which appears from this to be less stable than the bromo-salt described above.

The substitution of an iodide for the bromide has not led to the formation of an iodoplatinate; the iodine being immediately displaced by the acid action of the melted sulphate and the intervening action of the air.

If the sulphate of ammonium (which when hot is really equivalent to a bi-sulphate) is replaced by bi-sulphate of potassium, we obtain a bromoplatinate of potassium; but the return is bad, the greater part of the bromine going off in the state of hydrobromic acid and free bromine. Further, the bromoplatinate of potassium is slightly soluble in salts of potassium, which renders the separation difficult, and it is no good attempting to make the salt insoluble by means of sulphate of ammonium, this latter having the curious property of acting on the bromoplatinate of potassium, and converting it into an ammonium salt. The mixture of bisulphate and chloride of potassium gives potassic chloroplatinate, but the operation is not practicable, and further, it is of no particular interest.

The reaction of the mixture of sulphates and bromide of ammonium or potassium on platinum is well defined and practicable; it has, further, a definite, specific character.—*Comptes Rendus*, cxxv., No. 24, 1897.

ON PHOSPHOROUS OXIDE.

By A. BESSON.

I RECENTLY described the action which takes place in the cold between PCl_3 and crystallised PO_3H_3,—viz., disengagement of HCl and the formation of a syrupy liquid of an ill-defined composition, but which still remains stable when in contact with an excess of PCl_3.

When warmed the reaction is more complete, and leads to the formation of a reddish yellow solid body, which is nothing else than phosphorous oxide, P_2O, which I have already described in a previous communication as resulting from the reaction between PH_4Br and $POCl_3$.

If a concentrated solution of PO_3H_3, charged with an excess of PCl_3, be heated on a water-bath at about 100°, in a flask furnished with a vertical condenser, there is a continuous disengagement of HCl, and the formation in the mass of the solution of the PO_3H_3, which gradually thickens, of a solid body, bright yellow when in small particles and reddish yellow when in more considerable quantity. By continuing the operation, the syrupy mass becomes so thick that it is necessary to keep it constantly stirring, in order to renew the surfaces of contact. If, finally, we continue the reaction until cold, a solid, white, pulverulent body is formed, having the appearance of P_2O_5. When the reaction is complete, and after cooling, we add water carefully, as its addition is accompanied with a considerable disengagement of heat, and sometimes by a sound analogous to that which accompanies the hydration of P_2O_5.

The aqueous solution holds the reddish solid body in suspension; this is filtered off, washed with cold water, and dried *in vacuo* in the cold: this is the phosphorous oxide, P_2O, which is by this means obtained in a very pure state.

The analysis of two separate samples from different operations gave the following results :—

P per cent	79·37 and 80·06
P theoretically	79·49

The mechanism of the reactions may be conceived to be as follows :—PCl_3 reacting on PO_3H_4 would give P_2O_3, which would eventually decompose into P_2O and P_2O_5: this idea is in conformity with observations, and can be demonstrated by the two equations—

$$PCl_3 + PO_3H_3 = 3HCl + P_2O_3,$$
$$2P_2O_3 = P_2O + P_2O_5,$$

and it is to the formation of this latter body that the appearance, at the end of the reaction, of a solid white body is due, and also the disengagement of the greater part of the heat when water is added. It becomes therefore of importance to operate at as low a temperature as possible.

Phosphorous oxide is also formed by the direct oxidation of phosphorus under the following circumstances :—

A current of perfectly dry air is passed slowly through a solution of phosphorus in tetrachloride of carbon, the solution being protected from the light; chloride of carbon saturated with phosphorus at 30° to 40° might be used, and the oxidation carried on in the cold or in a tepid water-bath.

A yellowish white flocculent deposit soon appears, which soon thickens the solution. The liquid is then driven off over the water-bath, in a current of carbonic acid; the residue is washed with warm sulphide of carbon, of which the final traces are driven off in a current of CO_2.

It is then carefully treated with water; part of the material is dissolved with disengagement of heat, the whole is thrown on a filter and a yellow matter is left, which is washed first with warm water and then with cold, and afterwards dried *in vacuo*. The material thus separated is nothing else than phosphorous oxide, as is shown by the following analysis :—

P per cent	78·85 and 79·10
P theoretically	79·49

It has all the chemical and physical characteristics of, and behaves quite in the same way as, the body previously described. In fine, phosphorous oxide, P_2O, forms the major part of the impure product called *red oxide* or *yellow oxide*, and which contains either amorphous phosphorus or solid phosphide of hydrogen.—*Comptes Rendus*, vol. cxxv., No. 24, 1897.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

FIRST PAPER.—THE ANALYSIS OF COBALTOUS BROMIDE.

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

Introduction.

SIMULTANEOUSLY with the work described in a previous paper ("A Revision of the Atomic Weight of Nickel," *Proc. Amer. Acad.*, xxxiii., No. 7; CHEMICAL NEWS, lxxvi., p. 284) a similar investigation of cobalt was in progress. Earlier work upon this metal had led to results quite as incapable of ready interpretation as those concerning nickel; even very recent work upon the atomic weight of cobalt allows a range of much over a unit (from 58·78 to 60·1) as the possible field within which the truth may lie. Professor Clarke has given a full summary of all the available data upon this subject in his recent work (Smithsonian Miscellaneous Collections, "Constants of Nature," Part V., p. 291) upon the Re-calculation of the Atomic Weights, and for references and details the reader is referred to this useful volume. A chronological list is reprinted here merely to show how urgent is the need for further labour.

Earlier Work on Cobalt.

(O = 16).

			Atomic weight.
1826	Rothoff ..	CoO : 2AgCl	58·50
1857	Schneider ..	From cobaltous oxalate	60·00
1858	Marignac ..	$CoSO_4$: CoO	58·76
1858	„ ..	$CoCl_2$: 2Ag	58·85
1860	Dumas . ..	$CoCl_2$: 2Ag	59·09
1863	Russell . ..	CoO : Co	58·74
1867	„ . ..	Co : H_2 (measured) ..	59·08
1866	Sommaruga .	$Co_2(NH_3)_{10}Cl_6$: 2Co ..	59·95
1867	Winkler. ..	3Co : 2Au	59·42

* Contribution from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiii., No. 7.

			Atomic weight.
1868	Weselsky ..	From complex cyanides	59·13
1871	Lee (under W. Gibbs) ..	From complex cyanides	59·20
1871	Lee (under W. Gibbs) ..	$Co_2(NH_3)_{10}Cl_6 : 2Co$ ..	59·16
1886	Zimmermann	CoO : Co	58·89
1889	Winkler		
1891	Remmler ..	CoO : Co	58·80
1892	Schützenberger ..	CoO : Co	60·12
1893	Winkler ..	Co : 2Ag : 2AgCl	59·82
1894	,, ..	Co : I_2	59·52
1895	Hempel and Thiele ..	CoO : Co	58·99
1895	Hempel and Thiele ..	Co : Cl_2	58·78
1895	Hempel and Thiele ..	Co : 2AgCl	58·91

From these absurdly varsing results, Clarke (*Loc. cit.*) computes the value 58·932 as the most probable atomic weight, while Seubert (*Zeit. Anorg. Chem.*, xiii., 229) selects 59·6, and Ostwald ("Lehrbuch," vol. i., p. 79) 59·0, as the true value. Of course, many of the figures above may be thrown out at once; but the evidence which remains after this first elimination is still too vague for anything like scientific certainty. It is not the purpose of the present work to discuss the accuracy of these bygone investigations; for such discussions are apt to be unconvincing. Inattention to a single matter of detail may easily overthrow all the value of quantitative labour; a post-mortem examination is not always able to detect the more subtle poisons. Our object is rather to accumulate a mass of data which we thoroughly understand, and then to interpret these data with regard to the probable chemical errors which may have crept into them. The present paper is only the first one of an investigation which we hope to continue until we have solved the problem.

The advantages to be gained by a simultaneous investigation of nickel and cobalt are obvious. Although the similarity of the two metals is usually overrated, it is still convenient to consider them together. Evidently much time may be saved in the preparation of materials if two similar researches are conducted side by side; and evidently the experience gained in one may be immediately helpful in the other. Fortunately, cobalt, like nickel, yields a bromide which is readily obtained anhydrous in a state of great purity, and this metal therefore joins the ranks of those elements whose atomic weights may be determined by reference to silver through the most satisfactory of all processes of precipitation.

The Preparation and Properties of Cobaltous Bromide.

All the cobaltous bromide used in this research was prepared by passing bromine vapour over hot spongy cobalt. The sublimation of the salt is much less troublesome than that of the corresponding salt of nickel. The bright green anhydrous crystals of cobaltous bromide are very much less easily decomposed than the brown nickel compound by water or oxygen at a high temperature, in spite of the fact that cobaltous bromide is very much the more hygroscopic and soluble in water when cold. In no case was a trace of an oxide of cobalt found among the crystals of bromide used for the analyses.

The first experiments were carried on in a hard glass tube heated by a "combustion" furnace, but as the high heat necessary to volatilize cobalt bromide played sad havoc with the glass, porcelain tubes, heated by means of a perforated Fletcher furnace (*Proc. Amer. Acad.*, xxxii., 63), were substituted. The arrangement was similar to that used in the research upon nickel. Into one end of a large porcelain tube (of which the internal diameter was 28 millimetres) was ground a glass connector fused to the apparatus for supplying a mixture of bromine vapour, hydrobromic acid, and nitrogen; while inside of the other end was "telescoped" a closely fitting smaller porcelain tube designed to serve as the receiver of the sublimed material. The boat containing the cobalt was of course placed in the hottest part of the furnace, and the open end of the inner tube was adjusted just beyond this point. At first the glaze of the receiver tube was attacked by the hot bromine and bromides, and the first sample of sublimate was found to be contaminated by the decomposition products of the glaze. Later the porcelain became covered with a brilliant-coloured coating of a cobalt glaze which seemed to be permanent. The sublimate used in the analyses was taken more especially from the central portions of the sublimed masses, so that even if a small amount of alkali had been extracted from the porcelain it must have remained clinging to the walls of the tube. All the sublimates excepting the very first gave a wholly clear aqueous solution.

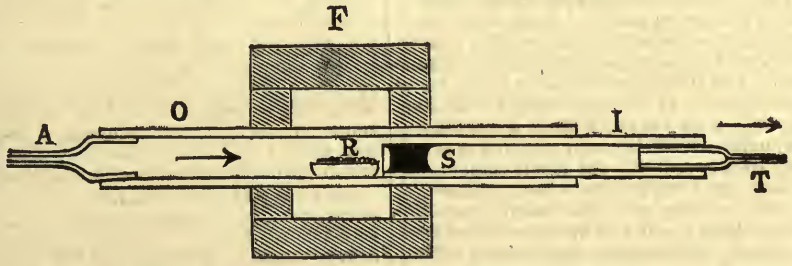


Fig. 1.—Section of Apparatus for Sublimation.
A, Glass tube for admitting bromine vapour. O, Outer porcelain tube. I, Inner porcelain tube. T, Glass outlet tube. F, Perforated Fletcher furnace. R, Boat containing cobalt. S, Sublimed bromide.

As has been already stated, anhydrous cobaltous bromide thus prepared consists of brilliant green crystalline plates, which quickly absorb water from the air to form the pink hydrated salt, and dissolve with great ease in cold water.

The specific gravity of anhydrous cobaltous bromide being unknown, the following experiments were made to determine it. (*a*) 2·0915 grms. of the salt which had been dried at about 200° displaced 0·3285 grm. of kerosene (dried over soda and re-distilled) at 25°. (*b*) 1·3965 grms. of the salt displaced 0·2186 grm. of kerosene. The kerosene, which was used in this case because cobaltous bromide was found to be slightly soluble in toluol, had at 25° a specific gravity of 0·7698 referred to water at 4°. Hence we have for the specific gravity sought, (*a*) 4·901, (*b*) 4·917. The mean of these two values is 4·909.

Since brass weights were employed, in order to correct the weights of cobaltous bromide found in air during the subsequent accurate analyses to that which would have been observed in a vacuum, 0·00010 grm. should be added for each grm. of this material. In the same way 0·000045 grm. must be added to every apparent grm. of argentic

bromide, and 0·000031 grm. must be subtracted from every apparent grm. of silver. These corrections are all applied below.

The balance used in this research was the one used in those upon copper, barium, strontium, zinc, and nickel: it needs no further description. The weights were of brass, gold plated; they were standardised with great care, and were used for no other work.

Purification of Materials.

Cobalt.—The doubt which has been thrown on the elementary character of cobalt by several experimenters led us to the application of unusual care in preparing the material used in this investigation. Pure cobalt was prepared by two entirely different methods, and a third sample was purified by both methods. The agreement of the results obtained from all of these samples leaves no doubt as to the uniformity of the material used.

In the first place about three hundred grms. of commercial cobalt chloride were dissolved in a litre of water. The removal of the copper group as sulphides was of course the first step, but on account of the difficulty of filtering out small quantities of these sulphides, the solution was not acidified before passing in sulphuretted hydrogen. In this way enough cobalt sulphide was precipitated to sweep the solution free from small amounts of a precipitate which could not be removed by filtration. After long standing the supernatant liquid was decanted through a filter, and as the precipitate was found to contain copper the solution was again fractionated with sulphuretted hydrogen. The sulphides from this precipitation gave no test for copper, hence it is fair to conclude that the filtrate was free from this metal. After the addition of a large amount of hydrochloric acid to this filtrate, and then ammonic hydrate until the mixture was strongly alkaline, pure sulphuretted hydrogen in excess was passed into the solution. The precipitated sulphides were washed several times with water, and then digested with cold dilute hydrochloric acid. The precipitate was then washed free from iron by decantation. As the succeeding purification by means of potassic nitrite was in itself a separation from many other metals as well as from nickel, it was not thought necessary to re-precipitate the cobalt sulphide at this stage. Accordingly the precipitate was dissolved in aqua regia, and after dilution and filtration the solution was evaporated until the greater part of the excess of acid was driven off. Sodic hydrate was then added to the diluted solution in slight excess, and subsequently a large amount of acetic acid. Upon the addition of potassic nitrate all the cobalt was precipitated as the crystalline yellow double nitrite of potassium and cobalt. This precipitate was washed by decantation several times, and after its solution in strong hot hydrochloric acid the precipitation was repeated. The reagents used in this purification were especially tested for calcium; for only in the absence of calcium is the separation of cobalt from nickel compete by this method. The efficiency of the separation is shown by the fact that the filtrate from the first precipitation was distinctly green, owing to the nickel salts present, while the filtrate from the second precipitation after evaporation to small volume merely turned faintly brown on the addition of ammonic sulphide. The double nitrite was again dissolved in hydrochloric acid, and the cobalt was partially freed from alkalis by precipitation as sulphide. The sulphide was then treated with an excess of nitric acid, and was heated upon the steam-bath until the resulting cobalt nitrate was free from every trace of chlorine.

In order to free the cobalt from alkalis it was next to be precipitated by electrolysis; and at first we hoped to convert the electrolytic film directly into bromide. However, on passing a galvanic current through the ammoniacal nitrate, an oxy-amine was precipitated in such quantities as to render the use of this electrolyte impossible. Experiments were then made with the ammoniacal sulphate in order to find the conditions most favourable for the deposition of a bright coherent film. The negative electrode was a plantinum dish, the positive electrode a flat spiral of platinum wire. The first attempts, which were made in a dish holding 250 c.c. and having an area of 150 square centimeters, with currents from 0·3 to 0·7 ampère, and with solutions of widely varying strengths, resulted in the deposition of dull black films. With a current strength of more than one ampère, however, the film was always comparatively bright. It was found impracticable to use this film directly for conversion into bromide on account of the difficulty of stripping the film from the dish. Accordingly, after being thoroughly washed, it was dissolved in the dish by nitric acid which had been distilled with a plantinum condenser; and when the excess of acid had been driven off by evaporation, a slight excess of pure ammonia (made by distilling ordinary pure ammonia into pure water contained in a platinum dish) was added. The resulting green precipitate was washed several times by decantation with the purest water, filtered on a washed filter, dried in a steam oven, and finally, after separation from the filter paper, ignited to the black oxide in a platinum crucible. During the ignition this crucible was contained in a porcelain crucible which was heated by an alcohol lamp. Pure metallic cobalt was prepared from this oxide by reduction in a stream of ammonia gas, generated in an apparatus composed entirely of glass and dried by passage over stick-soda. Metallic cobalt is thus obtained in a spongy form, well adapted for its following treatment with bromine, and certainly free from all such impurities as alkalis and silica. The cobalt bromide, prepared from this metal in the manner already described, was labelled No. I.

The second method of preparing pure cobalt was by precipitation as one of its amines. The purpureo-chloride seemed best suited for the present purpose, both on account of the ease with which it can be prepared, and because of its comparative insolubility in cold ammoniacal or acid solutions. At first this compound was made by passing a current of air for some time through a solution containing cobaltous chloride, ammonic chloride, and ammonia. A considerable quantity of purpureo-chloride was formed by this process, and from the solution, by acidification with hydrochloric acid and cooling, fully as much more was obtained. Later another method, capable of giving a much larger yield, was used. Into the strongly ammoniacal solution bromine was dropped slowly. A heavy precipitate resulted, and the solution upon acidification and cooling as above yielded the greater part of the cobalt it contained. Several lots of amines which had been prepared in one or the other of these ways were mixed and dissolved in hot ammonia. After filtering, the solution was acidified with hydrochloric acid, with the result that on cooling nearly all the cobalt was re-precipitated. The precipitate was washed by decantation with cold dilute hydrochloric acid, and the whole process of re-crystallisation repeated. This time the precipitate was collected on a pure filter and dried. After separation from the filter paper it was converted into the sulphates of cobalt and ammonium by heating on a sand-bath with sulphuric acid until all chlorine or hydrochloric acid fumes had ceased to come off. From the solution of these sulphates metallic cobalt was prepared by electrolysis, solution in nitric acid, precipitation as hydrate, and reduction, in the manner already described. This preparation was designated as Sample II.

For the final analyses the cobalt was purified by a combination of all the before-mentioned methods. The carefully purified cobaltous nitrate from Sample I. was converted into a cobaltamine compound, and this salt was six times re-crystallised by solution in ammonia and precipitation with hydrochloric acid. Each time the precipitate was washed twice by decantation with hydrochloric acid, and after the second, fourth, and sixth dissolving the ammoniacal solution was filtered. The final precipitate was converted into spongy metallic cobalt in the usual manner. After sublimation part of the

bromide prepared from this cobalt was re-sublimed to see if this process had any influence on the salt. That which had been re-sublimed was labelled IV., the other III. The apparatus used for the sublimation has been already described.

Silver was prepared with great care, according to a method similar to that described in previous papers from this Laboratory (*Proc. Amer. Acad.*, xxxii., 62). The only improvement introduced was the removal by means of nitric acid of the surface of the buttons, which had been fused in a vacuum upon a boat of lime. This treatment is of course more thorough and satisfactory than Stas's method of digesting them with hydrochloric acid. The silver was subsequently treated with ammonia, thoroughly washed with water, and dried in a desiccator over soda-lime. One large piece was rolled out between clean steel rollers; and the foil, after having been cut into small strips, was cleansed as above described. These fragments made it possible to weigh out any desired amount of the metal.

Bromine was prepared in common with Mr. Cushman. For the method used the paper upon nickel should be consulted. Much experience has led to the conclusion that the method there described is the most satisfactory and convenient means of obtaining pure bromine, since it eliminates organic as well as inorganic impurities. In order to test the purity of the bromine and silver, 2·18679 grms. of silver (in vacuum) were dissolved in pure nitic acid and precipitated with a slight excess of ammonic bromide which had been prepared by running the bromine in question into pure ammonia. The silver bromide was collected on a Gooch crucible and afterwards fused in a porcelain crucible. The fused bromide weighed 3·80679 in vacuum, whence the ratio of silver bromide to silver is 100·000 : 57·444. Mr. Cushman, experimenting upon the same sample of bromine, obtained the result 57·445 ; and since Stas's result was identical with these, there can be no doubt of the purity of our silver and bromine.

The sulphuric acid used in the drying towers was boiled for some time in order to increase its efficiency and to free it from volatile impurities. The phosphoric oxide was proved free from volatile compounds of phosphorus by passing a current of air over a considerable quantity of this substance in aqua regia for several hours. The aqua regia was subsequently found to contain no phosphorus. Distilled water was prepared with all the usual precautions necessary to free it from organic and non-volatile impurities, as well as from ammonia; nitric and hydrobromic acids were purified by repeated distillation with a platinum condenser; great care was taken to exclude dust, as well as the products of the combustion of illuminated gas, from the substances under treatment; platinum vessels were employed wherever it was possible to employ them; and many other precautions, often essential in order to prevent the complicated processes from introducing as much impurity as they removed, were applied. Alkali metals and silica, it will be seen, were among the impurities avoided as much as possible. For several pieces of platinum ware and other apparatus we are indebted to the Cyrus M. Warren Fund for research in Harvard University.

(To be continued).

NOTICES OF BOOKS.

Brewing Calculations: Gauging and Tables. By Claude E. Bater, M.A., F.C.S. London: E. and F. N. Spon, Lim. New York: Spon and Chamberlain. 1897.

In the convenient little pocket-book now before us may be found tables connected with brewing in all its branches. The author has endeavoured to do without algebraic formulæ as far as possible, so as to make the book of use to junior officials. There are also other tables, more of general than of technical interest, and a good index.

Transactions of the Institution of Mining and Metallurgy. Sixth Session. Vol. V. London: Broad Street House, E.C. 1897.

The fifth number of this publication is a bulky volume of 346 pages, edited by Arthur C. Claudet, A.R.S.M. It contains a goodly number of papers on different mining and metallurgical subjects, which have been read before the Institution during the past year. It is of interest to note that more than half the papers and notes are devoted to the various branches of gold mining and recovery.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxxv., No. 23, December 6, 1897.

Contamination of Wells.—M. Duclaux.—The proof of pollution is afforded by the appearance in the water of certain wells at Cantal of two elements almost absent in the virgin waters of the same geological region, *i.e.*, lime and chlorine.

Dissociation and Polymerisation of Gases and Vapours. Presumed Dissociation of Chlorine at Elevated Temperatures.—A. Leduc.—V. Meyer has announced that the molecule of chlorine undergoes a very important dissociation at high temperatures. Subsequently Crafts, whilst admitting the existence of this dissociation, declares it less powerful. The figures of M. Meyer, though not agreeing well, seem to indicate that it is the same at 900° and 1200°. The figure of M. Crafts at 1400° indicates an important dissociation.

Electric Conductivity of Discontinuous Conductive Substances with reference to Telegraphy without Wires.—E. Bronly.—This paper will be inserted at the earliest opportunity.

Transformation of the X Rays of Metals.—G. Sagnac.—The author shows that the X rays are diffused over polished metals without regular appreciable reflection. The rectilinear propogation, without any sensible diffraction of the secondary rays from metallic surfaces, can be easily demonstrated by receiving them on a photographic plate; these rays are also non-refrangible and are not reflected to any extent.

Some Novel Facts observed in Crookes Tubes.—Virgilio Machado.—If we pass the electric discharge of a Ruhmkorff coil into a Crookes tube a variety of interesting facts are observed. For instance, the shadow of an aluminium cross appears at the anti-cathodic part of the tube as well as in the ordinary manner. When the tube is brought near a magnet these two shadows separate, but the displacement of the secondary shadow is greater than that of the principal one.

Accidental Causes of Irreversibility in Chemical Reactions.—A. Colson.—The author has established that the mutual displacement of two acids—the one free and the other salified—is a reversible phenomenon governed by the laws of heterogeneous dissociation.

Existence of a Cuprous Sulphate.—A. Joannis.—Experiments indicate that cuprous sulphate exists in combination with both carbonic oxide and ammonia.

Elementary Unity of the Substance known as Cerium.—M. Wyrouboff and A. Verneuil.—A controversial paper on the elementary character of cerium.

Ammonium Aldehydate.—Marcel Delépine.—A Thermo-chemical paper on the representation of C_2H_7NO, *i.e.*, the ethylideneamine hydrate.

MISCELLANEOUS.

Royal Institution.—On Thursday next (January 20), Professor Dewar, F.R.S., will begin a course of three lectures at the Royal Institution on "The Halogen Group of Elements."

International Congress of Applied Chemistry.—The Honorary President of the Congress is Professor Dr. A. Bauer, the President is Dr. F. Perger, and the General Secretary is Dr. F. Strohmer. It is desired to form a committee of English chemists who are likely to be present at the Congress as representatives of England. Dr. F. M. Mrazsek will be happy to give any information about the Congress, including the best and cheapest routes to Vienna, the hotel accommodation, &c., and introductions to the members. He can be consulted personally at 29, Mincing Lane, between the hours of 10 and 5, or by letter.

City and Guilds of London Institute.—The report of the work of the Examination Deparment for the Session 1896-97 shows a marked increase not only in the number of classes, but also in the number of students and of candidates for examination. The past session has been marked by some extension of the Institute's work in India and the Colonies. Examinations have been held this year in New South Wales and New Zealand, and applications have been received for the holding of examinations in the colonies of Victoria and Queensland. The number of students in attendance during the year shows a very satisfactory increase, being 32,566 as against 29,494 in the previous year: 256 prizes have been awarded this year, comprising 227 money prizes, besides 103 silver and 153 bronze medals. Several changes have been introduced into the programme for the current session, especially with regard to textile subjects. Iron and steel manufacture has also received attention, modifications in the syllabus have been introduced having regard to local conditions of manufacture. Mine surveying, again, is being made more strictly technical; pure mathematics, which have nothing to do with the case, being omitted.

MEETINGS FOR THE WEEK.

TUESDAY, 18th.—Society of Arts, 4.30. "My Recent Journey from the Nile to Souakim," by Frederic Villiers.
—— Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LLD., F.R.S.
WEDNESDAY, 19th.—Society of Arts, 8. "The Projection of Luminous Objects in Space," by Eric Stuart Bruce, M.A.
—— Microscopical, 8. Annual Address of the President.
—— Institution of Mining and Metallurgy, 8. "Notes on the Action of Cyanogen on Gold," by James Park. "Mexican Methods of Mining," by S. B. Newall. "On the Successful Treatment of Tailings by the Direct Filling Process on the Witwatersrand," by F. Cardell Pengilly.
THURSDAY, 20th.—Chemical, 8. Ballot for the Election of Foreign Members. "The Action of Caustic Alkalis on Amides," by J. B. Cohen, Ph.D., and E. Brittain, B.Sc. "The Formstion of Monomethylaniline from Dimethylaniline," by J. B. Cohen, Ph.D., and H. T. Calvert, B.Sc. "Note on the Aluminium-mercury Couple," by J. B. Cohen, Ph.D., and H. T. Calvert, B.Sc. "Action of Chloroform and Alkaline Hydroxides on the Nitro-benzoic Acids," by W. J. Elliott, M.A. "Researches on the Terpenes—II., On the Oxidation of Fenchene," by J. A. Gardner, M.A., and G. B. Cockburn, B.A. "The Preparation of Pure Iodine," by B. Lean, D.Sc., and W. H. Whatmough.
—— Royal Institution, 3. "The Halogen Group of Elements," by Prof. Dewar, M.A., LL.D.
—— Society of Arts, 4.30. "Recreations of an Indian Official," by the Right Hon. Sir Mountstuart Elphinstone Grant Duff, G.C.S.I., C.I.E., F.R.S. (This meeting will be held in the East Conference Hall of the Imperial Institute, South Kensington).
FRIDAY, 21st.—Physical, 5. "On Electric Signalling without Conducting Wires," by Prof. O. Lodge, F.R.S. A Tesla Oscillator will be exhibited by Prof. S. P. Thompson, F.R.S.
—— Royal Institution, 9. "Buds and Stipules," by The Right Hon. Sir John Lubbock, Bart, M.P., D.C.L., LL.D., F.R.S.
SATURDAY, 22nd.—Royal Institution, 3. "Cyprus," by Prof. Patrick Geddes, F.R.S.E.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 1991.

AN IMPROVED SUPERHEATER FOR LABORATORY PURPOSES.

By J. ARTHUR WILSON.

For laboratory distillation with superheated steam the usual apparatus is a copper coil heated by a Bunsen burner. I have found this plan rather unreliable, as the temperature of the steam is subject to considerable fluctuation. A better plan, which gives very satisfactory results, is to place the coil in a copper cylindrical vessel containing paraffin-wax or similar body. The vessel is heated by a powerful burner, and the temperature equalised by a copper stirrer.

Newchurch, January 7, 1898.

A NOTE ON SOME FURTHER DETERMINATIONS OF THE DIELECTRIC CONSTANTS OF ORGANIC BODIES AND ELECTROLYTES AT VERY LOW TEMPERATURES.*

By JAMES DEWAR, M.A., LL.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution,
and
J. A. FLEMING, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London.

(Continued from p. 15).

We have, in addition, repeated and extended experiments made with the cone condenser on various electrolytes and dielectrics.

In the first place, we have carefully examined the effect of change of temperature on the dimensions of the cone condenser *per se* to ascertain if the dimensional change produced by cooling it in liquid air could sensibly affect the value of the dielectric constant of an electrolyte forming the dielectric between the cones, apart from the change which temperature produces in the dielectric quality of the dielectric itself.

The gilt cone condenser was accordingly connected with the tuning-fork interrupter as formerly described (see Fleming and Dewar, *Roy. Soc. Proc.*, lxi., 1897, p. 299), and the galvanometer scale deflection when the condenser was charged with 97·2 volts was found to be 3·85 c.m. to the left and 3·88 c.m. to the right,—hence the mean galvanometer deflection was 3·87 c.m. of the scale. This corrected to 100 volts becomes 3·98, and deducting 0·4 c.m. for the capacity of the leads gives 3·58 as the number representing the electrical capacity of the cone condenser as then arranged. A standard condenser belonging to the Davy-Faraday laboratory, and having a capacity of one-thousandth of a microfarad, was then substituted for the cone condenser, and gave right and left deflections of 19·1 and 19·6 c.m. respectively when charged with 97 volts. This corrected for capacity of leads (=0·4 c.m.) and reduced to 100 volts becomes 19·53. Hence, since the electrical capacities are proportional to the galvanometer deflection, the electrical capacity of our cone condenser is—

$$\frac{3.58}{19.53} \times 0.001$$

of a microfarad, or 0·000183 of a microfarad.

The capacity of the gilt cone condenser was then again measured with air at 20° C. as dielectric, and the galvanometer deflection observed. The outer cone was then cooled to −185° C. by quickly applying to it a large quantity of liquid air whilst the inner cone remained at about 20° C., and the galvanometer deflection again observed. This deflection was taken again when the inner cone had fallen in temperature to −75°, and finally when both inner and outer cones were at −185° C. The following numbers giving the galvanometer deflections are then proportional to the electrical capacity of the condenser between the cones.

Table V.—*Examination of the Effect of Cooling on the Electrical Capacity of the Cone Condenser.*

Galvanometer scale deflection in c.m. or electrical capacity of the cone condenser in arbitrary units, the dielectric being gaseous air.	Remarks.
4·22 c.m.	Inner and outer cones both at 20° C.
4·82 c.m.	Outer cone at −185° C. Inner cone at 20° C., about.
4·58 c.m.	Outer cone at −185° C. Inner cone at −75° C.
4·19 c.m.	Outer and inner cones both at −185° C.

Hence it is clear that mere change of temperature of the metal work of the cone condenser does not affect its electrical capacity by more than 1, or perhaps 2, per cent, and any larger changes in capacity found on cooling must be due to a real change in the dielectric constant of any dielectric substituted for the air between the cones, and not to mere dimensional changes of the condenser itself produced by the cooling.

Another matter to which our attention was directed was the question whether there was any sensible or serious lag in the temperature of the resistance thermometer behind the temperature of the dielectric. Our usual custom had been to immerse the condenser when prepared for use in liquid air, and cool down the whole mass to −185° C., and then raising it out of the liquid air to take temperature and capacity readings as it warmed up. The resistance thermometer was placed in the inner cone in a thin test-tube, and fixed in with fusible metal in the inner cone. We therefore tried one experiment with pure glycerin as dielectric, in which the electrical measurements were made as the condenser was slowly cooled, instead of being made as it slowly heated up. The process of cooling from −38° *pt.* to −201° *pt.* was allowed to occupy one hour and forty minutes. The values thus found for the dielectric constant for glycerin for this range of temperature were practically in agreement with those found when the condenser capacity was measured as it warmed up instead of cooled down.

Table VI.

I. *Dielectric Constant of Pure Glycerin.*

Corrected galvanometer deflection when the condenser had air as dielectric = 3·92 c.m. for 100 volts.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
− 38·0	2·85	50·5	Condenser charged with 1·434 volts. Time = 3.5 p.m.
− 42·6	2·97	52·8	
− 46·0	3·00	53·3	
− 55·8	3·17	56·5	
− 64·8	3·03	53·8	Time = 4.15 p.m.
− 98·8	2·70	3·95	Condenser charged with 17·0 volts.
−119·5	2·20	3·19	Time = 4.30 p.m.
−201·0	11·05	2·82	Condenser charged with 92·4 volts. Time = 4.45 p.m.

* A Paper read before the Royal Society, December 9th, 1897.

The above values of the dielectric constant of glycerin are in very fair agreement with the values obtained by us during rising temperature (*Roy. Soc. Proc.*, lxi., p. 324).

We have also extended our former obsevations made with this cone condenser and the galvanometric method to certain other frozen electrolytes, and measured their dielectric constants at low temperatures.

The results and substances are as follows :—

II. *Dielectric Constant of Dry Concentrated Sulphuric Acid* (H_2SO_4).

The corrected galvanometer deflection with air as dielectric was 3·92 c.m. for 100 volts. The switch frequency was 120.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
−200·9	14·6	3·86	Condenser charged with 94·2 volts.
−186·0	14·8	3·90	Condenser charged with 94·2 volts.
−181·8	2·5	3·82	Condenser charged with 16·2 volts.
−150·7	2·7	4·13	Condenser charged 16·2 volts.
−129·8	2·95	4·33	Condenser charged with 16·9 volts.
−110·0	6·0	7·25	Condenser charged with 17·0 volts.

III. *Dielectric Constant of Dry Concentrated Nitric Acid* (NO_3H).

Corrected galvanometer deflection with air as dielectric = 3·90 c.m. for 100 volts.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
−201·7	9·05	2·36	Condenser charged with 94·2 volts.
−182·7	9·27	2·46	
−165·8	9·25	2·42	
−118·2	9·40	2·45	
−129·7	10·00	2·62	

Before carrying out these experiments with the concentrated nitric and sulphuric acids the condenser had been carefully re-gilt, and a glass steady-pin substituted for the ebonite one.

IV. *Dielectric Constant of Sodium Fluoride* (NaF). (10 per cent solution).

Corrected galvanometer deflection with air as dielectric = 4·04 c.m. for 100 volts.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
−199·3	9·3	2·33	Condenser charged with 94·2 volts.
−174·2	9·3	2·35	
−149·2	10·35	2·55	
−135·0	14·35	3·67	
−125·0	19·6	5·05	
−115·7	4·4	7·07	Condenser charged with 15·2 volts.

The electrical resistance of the condenser at −200 *pt.* with frozen sodic fluoride as dielectric was 2000 megohms.

V. *Dielectric Constant of Hydrosodic Fluoride* (NaFHF). (10 per cent solution).

Corrected galvanometer deflection with air as dielectric = 3·42 c.m. for 100 volts.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
−201·8	8·87	2·28	
−186·0	8·87	2·25	
−169·0	8·95	2·30	
−178·8	9·0	2·31	
−148·8	9·7	2·49	
−142·2	10·9	2·79	
−131·5	15·4	4·02	

VI. *Dielectric Constant of Sodium Peroxide* (Na_2O_2). (5 per cent solution).

Corrected galvanometer deflection with air as dielectric = 4·41 c.m. for 100 volts.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
−198·0	4·5	71	Condenser charged 1·434 volts.
−184·5	5·5	87	

VII. *Dielectric Constant of Solution of Hydroxyl* (H_2O_2). (20 per cent solution by volume).

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
−203·5	10·8	2·38	Condenser charged with 99·2 volts.

Some experiments were then made by electrolysing freely certain electrolytes and freezing them with liquid air in the act of electrolysis. The dielectric constants were then subsequently determined in the frozen state.

VIII. *Dielectric Constants of Frozen Electrolytes, Electrolysed freely in the act of Freezing.*

Corrected galvanometer deflection with air as dielectric = 3·42 c.m. for 100 volts.

Temperature in platinum degrees.	Mean galvanometer deflection in centimetres.	Dielectric constant.	Observations.
	(*a*) 5 per cent aqueous solution of potassic hydrate electrolysed with 0·2 ampère and 8 volts. Evolved gas = 5·1 c.c.		
−200·0	3·85	71·4	Condenser charged with 1·434 volts. Electrical resistance of condenser 5000 megohms when frozen.
	(*b*) Water electrolysed with 1·0 ampère.		
−198·2	8·70	2·47	Condenser charged with 98 volts. Electrical resistance of condenser 5000 megohms when frozen.
	(*c*) Water electrolysed with 2·1 ampères.		
−198·0	8·65	2·42	Condenser charged with 98·9 volts.

It is evident that the action of electrolysis prior to and during freezing has no sensible effect on the subsequently measured dielectric constant, even though the surfaces of the cone condenser are strongly polarised in the act of freezing the liquid dielectric.

We have then paid some attention to the possible cause of the high dielectric values of some substances at very

low temperatures. It is clear from the above-described experiments with the Nernst bridge that for organic bodies such as ethylic alcohol, amyl alcohol, ethylic ether, and glycerin, we obtain practically the same dielectric values at the low temperature, both when they are measured by the galvanometric method with a switch frequency of 120 and when measured by Nernst's method with a frequency of 350, or about three times as great.

On the other hand, for certain other bodies, such as the frozen dilute hydrates of potassium and rubidium, and the oxide of copper suspended in ice, the dielectric value at the low temperatures is much diminished by increasing the frequency.

(To be continued).

ON CERIUM.

By M. BOUDOUARD.

In a note presented to the Académie (*Comptes Rendus*, vol. cxxv., p. 950) MM. Wyrouboff and Verneuil criticised the results I obtained with cerium (*Comptes Rendus*, vol. cxxv., p. 772).

1. While remarking on the difference in the origin of the oxides which were used by MM. Wyrouboff and Verneuil and myself, I will show, first of all, that my analytical results did not present between themselves any greater differences than those of these gentlemen.

MM. Wyrouboff and Verneuil pointed out as an *isolated* fact that in the fractionations of the sulphate the mother-liquors gave figures sometimes higher and sometimes lower than those furnished by the crystalline deposits. In their own determination we observe absolutely the same facts either in one way or the other.

For example, MM. Wyrouboff and Verneuil found:—

I. { 1st crystallisation 92·49 / 3rd " 92·76 } $d = 0{\cdot}27$; $e = \frac{0{\cdot}27}{92{\cdot}5} = 0{\cdot}0029$

II. { 1st " 92·56 / 3rd " 93·3 } $d = 0{\cdot}74$; $e = \frac{0{\cdot}74}{93} = 0{\cdot}0079$

For my part, I obtained—

I. { 1st crystallisation 136·5 / Mother-liquors 137·4 } $d = 0{\cdot}9$; $e = \frac{0{\cdot}9}{137} = 0{\cdot}0065$

II. { 1st crystallisation 137·15 / Mother-liquors 137·6 } $d = 0{\cdot}45$; $e = \frac{0{\cdot}45}{137} = 0{\cdot}0032$

III. { 1st crystallisation 137·85 / Mother-liquors 139·9 } $d = 2{\cdot}05$; $e = \frac{2{\cdot}05}{139} = 0{\cdot}0144$

Thus, MM. Wyrouboff and Verneuil qualify as *isolated* a fact given in my note, analagous results being also given in their memoir. I would remark that the error in both cases is equally great.

2. As to the difficultly acceptable observation that a cerium with an atomic weight of 137·85 has given two parts, of atomic weights of 140·7 and 138·5, that was a mistake on my part in writing the article only; there was nothing in common between the two series of determinations, and it should read—"Having made crystallisations of a sulphate prepared from a basic acetate," instead of "having made crystallisations of this same sulphate."

3. As to the action of peroxide of hydrogen on the acetate of cerium, as I always operated at a warm temperature I obtained a partial precipitation; that is, in fact, what I intended to do—it was not an error of observation. As to the purity of the oxide of cerium with which I worked, I believe it to be quite beyond criticism. MM. Wyrouboff and Verneuil insist that the criterion of purity of oxide of cerium is that it should be of a white colour; the oxide of cerium which I have obtained is white, and I took a great deal of trouble to free the cerium, not only from thorium, but from the other earths of the cerium and yttrium groups. I prepared the oxide of cerium by Debray's method, and it was the salts of this purified oxide that I fractionated.—*Comptes Rendus*, vol. cxxv., No. 25.

ON THE ANALYSIS OF SILICATES.

By A. LECLÈRE.

The principal difficulty in the analysis of silicates is in the passage of the silica through the gelatinous state. We well know that the evaporation to dryness, to which we ultimately have recourse, tends to the partial entanglement of the bases in the residue.

The analogies which exist between silicon, titanium, and tin would lead us to suppose that it is possible to obtain silica directly in the insoluble state by attacking a silicate, which would not become hydrated during its decomposition, with sufficiently concentrated nitric acid. We have proved that this result can be obtained by previously melting natural silicates with oxide of lead: this base, at a moderate temperature, forms very fusible compounds with all the elements found as silicates, and it retains the alkalis in a well-marked and characteristic manner.

It has been pointed out that the presence of oxide of lead is injurious to platinum vessels; but we have proved that platinum is in no way injured if we use pure oxide of lead, prepared in the manner which we shall presently describe, and also conduct the fusion in a muffle furnace in which any contact between the platinum and the gas flame is absolutely guarded against.

Porphyrised silicate is mixed with oxide of lead; a convenient quantity of oxide for a refractory clay is about three times the weight of the mineral, but the presence of alkalis enables us to reduce this proportion. We used a 40 m.m. platinum crucible weighing 4 grms., and provided with a cover. The fusion takes about half an hour in a muffle at a reddish orange heat, but if the silicate has not been finely powdered it is as well to prolong the fusion and add a little more oxide. By this means we obtain a liquid enamel which is easily detached from the platinum if we cool the underneath part quickly, taking care to keep the cover on, so as to avoid any loss by decrepitation.

This enamel is completely decomposed by a mixture, of not less than ten times its weight, of equal parts of ordinary nitric acid and fuming nitric acid. The attack should be made either in the cold or at about 40°, and if the enamel is first of all powdered it lasts about an hour; if, on the contrary, the pieces are comparatively large, the operation takes a longer time, even as long as one or two days. The attack is always complete, and leaves a residue composed of nitrate of lead and of completely insoluble hydrated silica.

Nothing now remains but to dilute with boiling water, which entirely dissolves the lead, and to collect the silica on a filter. The termination of the washing can be decided by means of a glass rod moistened with sulphide of ammonium, and the silica can be weighed after ignition at a high temperature.

The insoluble hydrate obtained by this method retains about 10 per cent of moisture when dried at 100°. If we operate on pure silica, and prepare the enamel in sufficiently thin sheets, so that there is no swelling under the action of the acid, we can obtain plates which show all the characteristic colours of the opal, after the solution of the nitrate of lead and the subsequent drying.

The acid liquor containing the nitrates is concentrated to get rid of the excess of nitric acid, and alcohol is then added. A quantity of hydrochloric acid, a little more than is necessary to precipitate the lead, is then added, and the lead separates immediately. The alcoholic liquor leaves on evaporation a residue, on which the estimation of the bases can be proceeded with by the well-known methods of Sainte-Claire Deville and M. Schlœsing.

The oxide of lead should be prepared according to the following method:—Into a 15 per cent solution of commercial nitrate of lead we pour a saturated solution of oxalic acid, containing also about 3 per cent of nitric acid. A very dense precipitate of oxalo-nitrate of lead is immediately formed, the impurities remaining in the acid solution. The precipitate is separated, dried in the oven, and calcined at a little below red heat in a porcelain crucible. About one-quarter of this is taken, moistened with nitric acid, and then ground up with the remainder. By repeating the calcination we obtain a finely-powdered minium, which constitutes the best form of lead oxide for the decomposiiton of silicates. — *Comptes Rendus*, vol. cxxv., No. 22.

ON THE DISSOCIATION SPECTRA OF MELTED SALTS.

METALLOIDS: CHLORINE, BROMINE, AND IODINE.

By A. de GRAMONT.

Chlorine.

The spectrum of free chlorine has been studied and measured by the late M. Salet in tubes at the ordinary pressure, excited by means of a spark from either an influence machine or a Ruhmkorff coil without a condenser. This question has also been studied by M. Thalén, and afterwards by M. Hasselberg under similar conditions, but with greater accuracy.

Having obtained, with the apparatus which I have already described in a previous paper, very excellent spectra of the lines of the metalloids in free air, without having recourse to Plücker or Salet tubes, but by the dissociation of melted salts under the influence of a condenser spark, I can now give the spectrum of chlorine produced by the principal alkaline chlorides, in which the small number of metallic lines renders the study much more simple. I still name the principal groups of lines by the Greek letters and the numbers used by M. Salet.

For comparing these figures with those of previous observers, I must refer my readers to a more extended memoir which I published in the *Annales de Chimie et de Physique*, Series 7, vol. x., Feb., 1897.

The following figures have been reduced to the normal spectrum of Rowland by means of a correction of +0·1.

Cl α		610·6	Doubtful.
Cl β	1.	545·7	Very well marked.
	2.	544·4	Fairly strong.
	3.	542·4	,, ,,
	4.	539·3	,, ,,
		532·6	Very faint; of doubtful origin.
Cl γ		522·1	Strong. } First principal group.
		521·7	,, }
Cl δ	1.	510·4	Fairly well seen.
		510·0	,, ,,
	2.	507·8	Easily seen.
		499·5	Fairly well seen.
		497·4	Rather weak.
Cl ε	1.	492·5	Weak.
		491·7	Easily seen.
	2.	490·4	Fairly strong.
	3.	489·8	,, ,,
Cl ζ		482·1	Strong; bright. } Second principal group.
		481·1	,, ,, }
		479·5	,, ,, }
		478·2	Well marked.
		476·9	,, ,,
		471·4	Faint.
Cl η		457·3	Diffuse; faint.

All the chlorides tried have given the lines of the spectrum of chlorine with the greatest facility, with the exception of those, of course, which were effaced by being in the immediate neighbourhood of, or in apparent coincidence with, the intense metallic lines, but these lines have been found by using different metals. The measurements were made with NaCl, LiCl, KCl, RbCl, $CdCl_2$, and $ZnCl_2$.

The Group Cl β is characteristic, and easily seen with even a small quantity of chlorine in the substance under examination. Cl γ—which is formed of two very bright strong lines, but which cannot be separated in an apparatus with only one prism—appears to be the most persistent both in duration and sensibility, and with Cl ζ the most characteristic. Cl δ, which is easily seen, is formed of three series; the first two of which appear as one with only one prism, are less visible than the third. The two most refrangible single lines of Cl ε are fairly bright. Cl ζ comes immediately after Cl γ in importance and duration, and is, in fact, of almost equal rank. This group ts essentially characteristic from the analytical point of view, and the most easy to recognise on account of the position of its three very strong and bright blue lines. Br μ, which occupies nearly the same position, consists of two lines only.

As a whole, the spectrum of chlorine is more beautiful, and the lines brighter and sharper, in melted chlorides with the condenser spark than in tubes with free chlorine, when they appear to be so diffuse that those nearest to each other cannot be separated.

As an example of the sensitiveness of the spectral reaction of chlorine by this method, we may mention this fact:—A bead of 0·02 grm. of Na_2CO_3, containing 0·0005 of chlorine added in the form of NaCl, gave all the lines of chlorine; with only 0·0001 grm. of chlorine the groups Cl γ and Cl ζ were still visible. Hydrogen prepared from hydrochloric acid and zinc will, when the flow of gas through the wash-bottles is too rapid, carry a certain amount of hydrochloric acid with it, the traces of which can be detected by the appearance of Cl γ.

Bromine.

Since the memoir published by Salet, in 1873, I am not aware that the spark spectrum of bromine has been the subject of any further research. Richer in lines than that of chlorine, it is also as bright and as easily observed in melted salts dissociated by the condenser spark.

I here give the wave-lengths measured with a direct-vision spectroscope with two prisms, and corrected to the normal spectrum of Rowland. The arrangement of the apparatus was the same as in the previously described experiments. (See Table, next column).

The Greek letters and the numbers used are the same as those of M. Salet. Br β, easily seen, is given by M. Salet as a triple line; he, however, only used a single prism. On the contrary, I, with my spectroscope with two fairly dispersive prisms, with a very narrow slit, and a very steady support, have never been able to see more than one line in this position; it is very sharp in melted bromides, but vague in a tube of free bromine. Again, Br γ, Br δ, and Br ε, described as double by M. Salet, have not been noticed as double by me under the conditions just described, although the very greatest care was used. The brilliancy of Br γ is slightly diminished by the almost inevitable presence of Na α. Br δ appears to be very much weakened in the condenser spark, and is difficult to see. The group Br ζ is very characteristic, and has two of its lines (ζ_3 and ζ_4) much more persistent than the others. Br η and Br θ appear to be much brighter than they were described by M. Salet.] The two characteristic lines Br μ are very distinctive of bromine, although they are very close neighbours of some of the chlorine lines, which actually has one in between the two. Br ν, which is very strong, appears to be the most persistent in the case of only a very small percentage of bromine being present in the salt under examination. Br π, easy to see, terminates the visible spectrum of bromine under the conditions in which

Br α		632·5	Well marked.
Br β		614·7	Easily seen.
		587·1	Faint; doubtful.
Br γ		583·05	Well marked.
Br δ		572·0	Very faint.
Br ϵ		559·05	Well marked.
		551·1	Easily seen.
		549·85	,, ,,
		549·2	,, ,,
		544·8	Faint.
		543·6	Fairly well seen.
		542·5	Easily seen.
Br ζ	1.	533·2	Very strong.
	2.	530·5	Strong.
	3.	523·75	Very strong.
	4.	518·35	,, ,,
	5.	516·5	Well marked.
		510·75	Fairly strong, but variable.
Br η		505·5	Well marked.
Br θ		493·0	Fairly strong.
Br μ	1.	481·7	Very strong.
	2.	478·7	,, ,,
		476·8	Easily seen.
		474·4	,, ,,
		472·1	,, ,,
Br ν		470·45	Very strong.
		469·25	Fairly well seen.
		467·75	Fairly strong.
		462·3	Easily seen.
Br π		436·55	,, ,,

I worked. The most characteristic groups of this metalloid in melted salts are therefore:—

Of first rank .. .. Br ν, Br μ.
Of second rank .. .. Br ζ.

The measurements were made on NaBr, KBr, $CaBr_2$, $ZnBr_2$. The sensitiveness of the spectral reaction of bromine seems to be equal to that of chlorine, and has been similarly used in analysis.

Iodine.

Like bromine, iodine has not been studied since the research of M. Salet on the spark spectrum with an ordinary monoprismatic spectroscope. I here give the spectrum of this body obtained by the dissociation of NaI, KI, and CdI_2, with the condenser spark, and my usual apparatus, and spectroscope.

The wave-lengths have been corrected for the normal spectrum of Rowland:—

		625·8	Fairly well marked
		620·7	,,
I α		612·7	Very well marked.
I β		608·6	Fairly visible.
		607·7	Fairly strong.
I γ		595·1	Strong.
		578·9	Fairly visible.
I δ	1.	577·55	Well marked.
	2.	576·1	Fairly well marked.
	3.	573·85	Well marked.
	4.	571·0	,,
		569·2	Fairly well marked.
	5.	567·85	Well marked.
I ϵ		562·7	,,
		561·4	Very faint.
		560·2	Faint.
		559·6	,,
		555·4	Very faint.
		552·5	,,
		550·8	Faint.
I ζ	1.	549·9	Strong.
		549·6	Well seen.
	2.	546·6	Very strong.
	3.	543·8	Strong.
	4.	540·5	,,
		537·0	Fairly strong.
I η	1.	534·4	Very strong.
	2.	533·75	,,
		526·8	Well seen.
		526·45	Fairly well seen.
I θ		524·55	Well marked.
		521·65	,,
		517·65	Faint.
I μ		516·25	Very strong.
		510·7	Well marked.
I ν		506·6	Fairly well seen.
I ξ	1.	486·5	Well seen; diffuse.
	2.	485·05	,, ,,
		480·55	Faint.
		476·6	,,
		473·25	,,
I o		467·75	Well marked.
		466·8	,,
I π		464·25	,,
		463·2	,,
		462·3	,,
I ρ		445·4	Fairly well seen; diffuse.
		445·0	,, ,,
		444·0	Rather faint; diffuse.
		441·15	Faint; diffuse.
I σ		422·5	Well seen.

As is at once seen, this spectrum is richer in lines than those of both chlorine and bromine, particularly in the orange red. The principal lines in this region, I α, I β, I γ, are easily seen, even with a low proportion of iodide in the salt under examination—a fact which does not apply to the two red lines in the bromine spectrum. I δ, formed of seven lines, is not particularly bright. I ϵ is, on the contrary, very bright, as is also the group I ζ_2, and especially the line ζ_2 (546·6).

Chlorine has a group (Cl β) almost corresponding in appearance and position with I ζ, but it is not so bright, and the lines are not so wide apart as in the latter case. I give 549·6 with all reserve, because of the air line 549·66 (Néovius), although the air spectrum was not apparent at the time of the observation. I η, consisting of two brilliant lines, and the strong line I μ, are the most remarkable in the spectrum of iodine, both by reason of their intensity and their sensitiveness in detecting minimal quantities of iodine. (521·65) almost coincides with Cl γ (521·70), the most sensitive group in the chlorine spectrum; but experience has shown that it is really due to iodine, where I have always found it of constant intensity, and unaccompanied by the other component (522·10) of Cl ζ. I θ, I ν, I σ, I ρ, and I o are well seen and of medium brilliancy, superior to the diffuse lines of the group I γ, which are often difficult to separate.

The most sensitive and characteristic groups or lines of iodine in melted salts are therefore:—

Of first rank .. .. I η, I μ, I ζ_2.
Of second rank .. .. I ζ (as a whole), I ϵ, I α, I β, I γ.

The spectral sensitiveness of iodine, tested by the method already used for chlorine, seems to be about the same.—*Bull. Soc. Chimie.*, Series 3, vol. xvii-xviii., No. 20.

A Coloured Reaction of Ordinary Aldehyd.—Louis Simon.—The property of producing a beautiful red colouration with nitro-prussiate of sodium and potash, either with or without the subsequent addition of acetic acid, is shared by ordinary ethylic aldehyd with a large number of aldehydic and ketonic bodies; but, on the other hand, the following reaction, viz., adding a few drops of aqueous methylamine and a few drops of dilute nitroprussiate to a weak solution of ordinary ethylic aldehyd, gives a beautiful blue colour which is quite characteristic.—*Comptes Rendus*, cxxv., No. 25.

A REVISION OF THE ATOMIC WEIGHT OF COBALT.*

FIRST PAPER.—THE ANALYSIS OF COBALTOUS BROMIDE.

By THEODORE WILLIAM RICHARDS
and
GREGORY PAUL BAXTER.

(Concluded from p. 23).

The Method of Analysis.

THE most insidious of all impurities in accurate quantitative work is water. Its insidiousness is due to the difficulty of detecting it in small amounts, as well as to its invariable occurrence in the atmosphere and its common use as a solvent and medium for crystallisation. Our first analytical problem, in this case just as in the case of nickel, was to weigh the salt to be analysed in such a fashion as to exclude this ever watchful enemy. The fact that cobaltous bromide is less easily decomposed at high temperatures than is nickelous bromide, tended to make our present problem the easier of the two; but the much greater hygroscopicity of the cobalt salt had the opposite tendency. The apparatus so useful in the cases of magnesium (Richards and Parker, *Proc. Amer. Acad.*, xxxii., 59), zinc, and nickel (Richards and Cushman, *Proc. Amer. Acad.*, xxxiii., p. 95; CHEM. NEWS, lxxvi., p. 284), proved to be equally serviceable here; cobaltous bromide, after being ignited in a stream of mixed nitrogen and hydrobromic acid, cooled in dry nitrogen, and bottled automatically in dry air, may be weighed with perfect certainty. The bottling apparatus has been described so often that further details are unnecessary here; but the apparatus for supplying the desired gases has not yet been explained in all the complication of its present form.

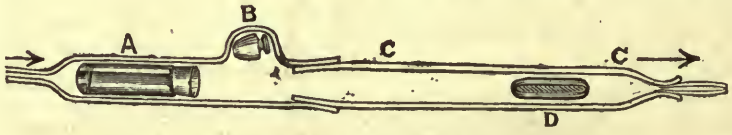

FIG. 2.—BOTTLING APPARATUS, HORIZONTAL SECTION.

A, Weighing bottle B, Stopper of bottle. C C, Hard glass tube. D, Platinum boat containing cobaltous bromide.

In the first place, nitrogen was prepared by passing air through strong ammonia water, and then over red-hot copper. The nitrogen, after passing through several flasks of sulphuric acid to remove the excess of ammonia, was conducted into column 1 (see Fig. 3), containing beads soaked with silver nitrate, in order to free the gas from the possible admixture of sulphur compounds taken from the rubber connections which were used in the apparatus for making nitrogen. In the columns numbered 2 were beads drenched with strong sulphuric acid, which thoroughly dried the nitrogen. With stopcock 12 open, the nitrogen passed over phosphoric anhydride in tube 11 directly into the bottling tube. With stopcock 12 closed and 4 open, the nitrogen of necessity bubbled through bromine in the small flask 5; beyond this flask, if stop cock 9 were open, the gases passed directly over phosphoric anhydride in 10 to the cobalt bromide; if stopcock 9 were closed, the nitrogen and bromine together passed into the flask 6, containing hydrobromic acid and red phosphorus, thence into the U-tube 7, containing beads moistened with hydrobromic acid and red phosphorus, thence over anhydrous calcic bromide in the tube 8 to remove the water taken from the hydrobromic acid, and finally over phosphoric anhydride in 10 to the bromide of cobalt. Dry air was prepared by passing a current of air through several columns of beads (O P in the figure) moistened with sulphuric acid, and then into the apparatus through the stopcock 14. The pressure of the sulphuric acid in the bulb 3 prevented any air from backing up into the sulphuric acid columns delivering nitrogen. In order to prevent the slightest admixture of hydrobromic acid with the dry air used to wash out the apparatus at the conclusion of the operation, a slight excess of pressure was always maintained within the apparatus. This excess of pressure was so regulated as to cause a part of the pure air to go backwards through tube 10 (stopcocks 4 and 9 being closed), and to bubble through the sulphuric acid kept in the vessel labelled 13. The tube and vessel served as a safety-value and pressure gauge throughout the whole operation. The ground joints were kept tight by means of syrupy phosphoric acid.

To the right hand end of the complex apparatus here described was fused the automatic bottling apparatus, as indicated in Fig. 3. By means of this arrangement the cobaltous bromide could be thoroughly dried, and enclosed in a suitable bottle for weighing without a moment's exposure to the moist air of the room. In one case, where a platinum boat containing several grms. of the salt was re-heated and re-bottled after weighing, the loss in weight was found to be only 0·11 milligrm., an amount not greater than the probable loss by sublimation at the high temperature (400°) employed in the ignition. Hence the apparatus evidently answers its purpose well.

The preliminary analyses were so much easier to make than those described in the preceding paper—because of the ready solubility of the salt used, and its invariable freedom from the oxide whose presence had caused trouble at first in the work upon nickel—that only three were deemed necessary.

The method of procedure may be easily gathered from previous descriptions. The bromides of cobalt and silver were each weighed, as in the case of the nickel, and from the assumed molecular weight of argentic bromide 187·885 that of cobaltous bromide was calculated.

From the value for the atomic weight of cobalt obtained from this preliminary series, the approximate proportion of silver necessary for the complete decomposition of a given weight of cobaltous bromide was calculated; and in the succeeding analyses the proper amount of silver was weighed out in each case. After the silver had been dissolved with precautions to prevent loss during the process, and after the solutions of cobaltous bromide and argentic nitrate had been much diluted, the precipitation was effected in a roomy, glass-stoppered Erlenmeyer flask, and the mixture was very thoroughly shaken and allowed to stand. In three experiments, Nos. 4, 6, and 7, the precipitation was completed by titrating backward and forward with centinormal argentic nitrate and hydrobromic acid solution, until the precise point was found (*Proc. Amer. Acad.*, xxviii., 24; xxx., 384); while in Nos. 8, 9, 11, 12, and 13 the nephelometer was used to determine the end-point (*Ibid.*, xxx., 385). Of course, the work was done in yellow light or in darkness, and great care was taken to prevent the loss of any of the precipitate. The results of this determination of the amount of silver required to precipitate the bromine in cobaltous bromide are given in the table headed, "Third Series," below. The "Second Series" of results was obtained by weighing the argentic bromide precipitated in the manner just described. Before filtering, a slight excess of argentic

* Contribution from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxiii., No. 7.

The Atomic Weight of Cobalt.
O = 16·000 ; Ag = 107·93.

First Series (Preliminary).—2AgBr ; $CoBr_2$.

Number of analysis.	Sample of $CoBr_2$.	Weight of cobaltous bromide in vacuum.	Weight of argentic bromide in vacuum.	Atomic weight of cobalt.
1.	I.	2·25295	3·86818	58·950
2.	I.	2·88763	4·95732	58·975
3.	I.	1·88806	3·24056	59·026
		Average		58·984

nitrate was added, and after long agitation the precipitate was collected as usual upon the Gooch crucible. The shreds of displaced asbestos were collected and weighed, and from the total was substracted the small amount (if any) of argentic bromide resulting from hydrobromic acid added in titration. One experiment (No. 5), in which the cobaltous bromide contained a few visible chips of porcelain from the tube used in subliming, was rejected; and in one (No. 10) the weight of the silver was not determined.

Second Series.—2AgBr : $CoBr_2$.

Number of analysis.	Sample of $CoBr_2$.	Weight of cobaltous bromide. in vacuum.	Weight of argentic bromide in vacuum.	Atomic weight of cobalt.
4.	I.	1·33564	2·29296	58·975
6.	I.	2·58129	4·43095	58·998
7.	I.	2·84382	4·88135	59·009
8.	I.	1·83722	3·15368	59·000
9.	I.	2·68584	4·61046	58·996
10.	II.	3·18990	5·47607	58·982
11.	II.	2·88914	4·95943	58·997
12.	III.	2·32840	3·99706	58·987
13.	IV.	1·91703	3·29053	59·010
		Average		58·995

Third Series.—2Ag : $CoBr_2$.

Number of analysis.	Sample of $CoBr_2$.	Weight of cobaltous bromide in vacuum.	Weight of silver in vacuum.	Atomic weight of cobalt.
4.	I.	1·33564	1·31702	59·002
6.	I.	2·58129	2·54585	58·955
7.	I.	2·84382	2·80449	58·977
8.	I.	1·83722	1·81170	58·991
9.	I.	2·68584	2·64879	58·969
11.	II.	2·88914	2·84891	58·998
12.	III.	2·32840	2·29593	59·003
13.	IV.	1·91703	1·89033	58·999
		Average		58·987
		Average of Series II. and III..		58·991

which were the most carefully made, the ratio becomes 57·446 : 100·000, while Stas's result is 57·445. The value of this comparison has been pointed out in the previous paper on nickel.

A still more important consideration is the indentity of

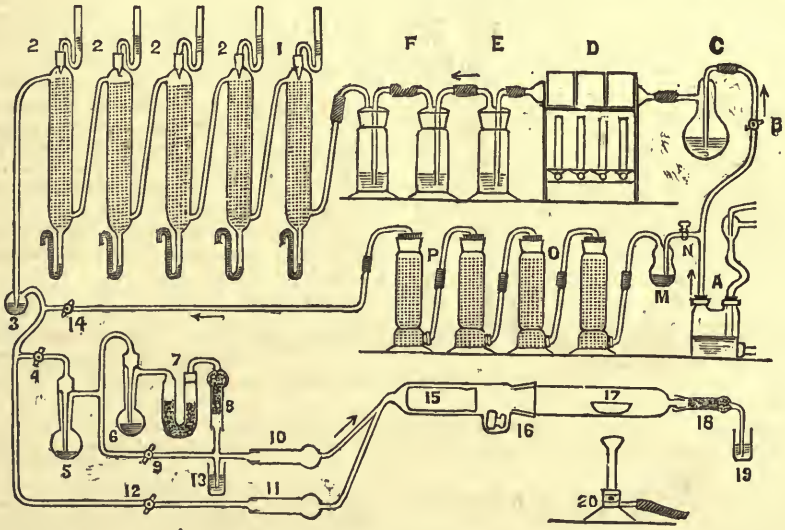

Fig. 3.—Apparatus for Igniting Cobaltous Bromide in any desired Mixture of Gases.
The use of rubber was confined to the first part of this train, where it could do no harm (A B C D E F and A M N O P).

As usual in cases of this sort, we may obtain a useful check upon the accuracy of these results by comparing the amount of silver required with the amount of argentic bromide formed. Thus, in all these experiments taken together 18·16302 grms. of silver yielded 31·61642 grms. of argentic bromide—a ratio of 57·448 to 100·000. If we take only the last five experiments (8, 9, 11, 12, and 13), the results obtained from the various samples. The average of all the results of each of the four preparations is given below—the first average comprehending ten results, the second three, and the third and fourth each two results :—

Sample I.	58·987
Sample II.	58·992
Sample III.	58·995
Sample IV.	59·004

In this case, as in the case of nickel, a slight rise in the atomic weight is to be observed with the increasing purity of the materials. Although larger here than before, the rise cannot be considered greater than the probable experimental error—especially since one or two of the individual results obtained from Sample I. were slightly greater than any obtained from Sample IV. We must therefore conclude that, if "gnomium" exists, it must have an atomic weight about equal to that of nickel and cobalt, and hence that the wide variations to be observed in the results of other experimenters cannot be considered a valid argument in favour of the late Professor Krüss's doubtful discovery.

According to the present investigation then, the atomic weight of cobalt seems to be very close to 59. Upon

comparing this result with the earlier ones of other experimenters, we see that it is as much in accord with their general verdict as almost any other would be. In other words, the values are so various in magnitude that no satisfactory conclusion can be drawn from them. It is worth noticing that one of the results obtained by Thiele, under Professor Hempel's direction, agrees exactly with ours, however.

Our work thus has this outcome at its present stage:—

If Oxygen = 16·000, Cobalt = 58·99.
If Oxygen = 15·88, Cobalt = 58·55.

PHOSPHORIC ACID DETERMINATION.*

A Gravimetric Method of Estimating Phosphoric Acid as Ammonium Phosphomolybdate.

By THOMAS S. GLADDING.

The estimation of phosphoric acid by weighing the yellow precipitate of ammonium phosphomolybdate has often been attempted, but, except in iron analysis, where the amount of phosphorus is very small, such a method has never yet been successful. The reason of such failure is evident when we consider the analyses that have been made of the yellow precipitate. A few only need be presented.

	Rammelsberg.	Struve and Svanberg.	Sonnenschein.	Gibbs.
H_2O	5·77	9·49	11·23	3·94
NH_4OH	3·25	9·49	11·23	3·35
P_2O_5	3·90	3·63	3·03	3·66
MoO_3	86·45	86·88	86·87	89·05

Gibbs gives the following formula for the salt:—

$$24MoO_3,P_2O_5,3(NH_4)_2O + \\ +24MoO_3,P_2O_52(NH_4)_2OH_2O+16Aq.$$

He prepared the salt by mixing solutions of ammonium molybdate (7 parts of water to 3 of the salt) and phosphate, adding nitric acid in excess to the solution, and boiling. Such a method would give more or less occluded molybdic oxide. His analyses gave 3·70 and 3·83 per cent of phosphorus pentoxide against the theoretical percentage of 3·66. Such results were sufficiently accurate for his purposes, but would discourage any suggestion of using the yellow salt as the basis of a gravimetric method. His formula is, however, without any doubt, the correct one, with the exception of the water of crystallisation.

My own analysis of the salt precipitated in the manner described later on, and dried at a temperature of 105° C. to a constant weight, gives me the following composition:—

	Theoretical.	By analysis.
$48MoO_3$	91·38	91·36
$2P_2O_5$	3·76	3·76
$10NH_3$	2·25	2·31
$11H_2O$	2·61	2·57

For ammonia, 1·015 grms. gave 0·0234 grm. NH_3 = 2·30 per cent.

For ammonia, 20·193 grms. gave 0·4690 grm. NH_3 = 2·32 per cent.

For moisture, 7·25 grms. gave ——— = 2·53 per cent.

For moisture, 10·30 grms. gave ——— = 2·61 per cent.

The water was determined by estimating total hydrogen by combustion with copper oxide.

For phosphoric acid, repeated analyses and syntheses gave almost exactly 3·76 per cent.

The molybdic acid was found by difference.

The fact that drying at 105° C. expels all the water except eleven molecules, and that the yellow salt when dried over sulphuric acid in a close desiccator comes to the same weight as when dried at 105° C. would indicate that this salt contains no other water of crystallisation. Any excess of water is apparently hygroscopic water and not water of crystallisation. I therefore find the following as the correct formula for the crystallised yellow salt:—

$$24MoO_3,P_2O_53(NH_4)_2O + \\ +24MoO_3,P_2O_5,2(NH_4)_2O.H_2O+5Aq.$$

The following method of procedure has given me a precipitate of a very uniform composition, and would seem to afford the simplest and easiest method yet presented for estimating phosphoric acid.

To the solution of phosphoric acid (25 c.c. to 50 c.c. in bulk) are added 25 c.c. of strong ammonia, 0·900 sp. gr.; nitric acid, 1·42 sp. gr., is now added to acidity. The beaker containing the solution is placed in a water-bath maintained at a constant temperature of 50° C. The ordinary five per cent acid molybdate solution is now added from a burette at the rate of about 3 drops per second, with constant stirring (50 c.c. may be added in five minutes). When the molybdate solution to an excess of about 10 c.c. has been added, the beaker is allowed to remain for ten minutes in the bath. The contents are then filtered through a weighed filtered paper.

The filtrate, without the washings, and after the addition of 5 c.c. molybdate solution, is replaced in the bath for ten minutes. The liquid should remain clear, or at most show only a faint opalescence.

For washing the precipitate, a wash water of dilute nitric acid 100:1 is employed. Three generous washings by decantation and three washings on the paper, followed by one final washing with distilled water are sufficient. The paper and contents are now drained for a few minutes on some waste filter or blotting paper, and then dried to a constant weight at a temperature of 105° C.

In this method the formation of a pure granular precipitate of uniform composition and free from occluded salts is secured by the gradual addition, drop by drop, of the molybdate solution with constant stirring. The completeness of precipitation of the phosphoric acid is attained by the presence of a large amount of ammonium nitrate. The separation of molybdic oxide or iron salt is avoided by the low temperature employed.

For the final drying at 105° C. an air-bath was tried and decisively abandoned. The use of a liquid boiling at 108° C. to 110° C. is the only safe course. A water-oven consisting of several distinct divisions or floors, one above the other, and surrounded with dilute glycerol, 1·160 sp. gr. boiling at 110° C., was found to work admirably. The lower bath or division is reserved for the final drying. None but dry or almost dry precipitates must be allowed in this lower division. The precipitate may be dried in an ordinary water-oven almost to a constant weight and then dried to constant weight in a glycerol oven at 105° C. The filter papers used are dried at 105° C. and weighed between large, closely fitting ground watch-glasses. The final weighings of papers and contents are made in the same manner.

The following investigation serves to show the results that are secured by this method of analysis.

A chemically pure microcosmic salt was finely pulverised. Careful ignition of 10 grms. in a covered platinum dish gave 4·8955 grms. of sodium phosphate, giving a percentage by calculation of 34·07 per cent phosphorus pentoxide. Ten grms. of the salt were now dissolved in 1 litre of water and aliquots taken. Twenty-five c.c. containing 0·250 grm. of microcosmic salt were treated exactly as above. Fifty c.c. containing 0·500 grm. microcosmic salt were treated by the official magnesia method. The following results were obtained:—

	Gladding method.		Magnesia method.
	Taken.	Per cent.	Taken.	Per cent.
1	0·250	34·07	0·500	34·07
2	0·250	34·08	0·500	34·05
3	0·250	34·06	0·500	34·09
4	0·250	34·10	0·500	34·08

* Read before the New York Section of the American Chemical Society. From the *American Fertiliser*.

A solution of one-tenth of the above strength was obtained by dilution. Of this the following quantities were used and the phoshporic acid therein obtained by the new method :—

	Taken. c.c.	Yellow salt. obtained.	Phosphorus pentoxide obtained.	Theoretical phosphorus pentoxide.
1	10	0·091	0·00342	0·003407
2	1	0·010	0·00037	0·00034

These last experiments demonstrate the insolubility of the yellow salt and the applicability of the new method to very small amounts of phosphoric acid.

A number of comparative tests of fertilisers gave closely agreeing results, as follows :—

	Official method. Per cent.	New method. Per cent.
Phosphoric acid ..	28·80	28·87
Phosphoric acid ..	2·63	2·70
Phosphoric acid ..	12·03	12·00
Phosphoric acid ..	28·30	28·33
Phosphoric acid ..	15·64	15·70
Phosphoric acid ..	15·04	15·00
Phosphoric acid ..	15·19	15·23
Phosphoric acid ..	29·16	29·23

In all fertiliser work 0·250 grm. was used for precipitation, and molybdate solution to an excess of about 10 c.c. was added. No more than 10 c.c. in excess should be used.

Tankages and fertilisers containing a notable amount of organic matter should be ignited before solution.

An application of this method to the direct determination of reverted or citrate soluble phosphoric acid promises good results. The method of procedure is as follows :—The citrate filtrate and washings are made up to 200 c.c. Twenty-five c.c., equivalent to 0·250 grm. of the fertilizer are treated as follows :—Fifty c.c. ammonia, 0·900 sp. gr., are added and then nitric acid to acidity. The liquid is now diluted to half a litre to overcome the solvent action of the ammonium citrate, and heated in a bath to 65° C. Fifty c.c. of molybdate solution are added in a thin stream with stirring, and the whole digested for 30 minutes. The rest of the analysis is conducted precisely as in ordinary work, except that the filtrate is heated for thirty minutes longer at 65° C. The liquid should remain clear.

The bath used for drying the precipitates is made of very heavy copper, with double turned joints, the three divisions, or floors, one above the other, are of the following :—Inside dimensions, 10 inches wide, 7 inches deep, and 4 inches high.

The two lower divisions are surrounded by the glycerol on all sides except the front; the level of the glycerol reaches to the middle of the upper division. The upper division answers for the preliminary drying, the two lower for the final and complete desiccation.

The following directions for fertilisers will be found useful :—

For 0·250 grm. of each of the following fertilisers use the following amounts of molybdate of ammonia solution :—

	P_2O_5 present. Grm.	Use of molybdate solution. C.c.
Tankage	0·020 to 0·040	25
Ground bone	0·060	40
Fish scrap	0·020	20
Rock phosphate (low grade)	0·065	40
Rock phosphate (high grade)	0·090	
Acid phosphate (total) ..	0·030 to 0·040	55
Superphosphate (total) ..	0·035	30
Bone-black	0·090	25
		55

All filtrates are to be carefully tested as directed. In filtering and washing the yellow salt, a suction pump is recommended. Two final washings (of 2 c.c. each) of alcohol will greatly lessen the time required for drying the precipitates.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1897.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 1st to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during December shows a small excess, the recorded amount being 2·50 inches, against a thirty-years' average of 2·10 inches; the excess is therefore 0·40 inch.

The details of the rainfall are shown in the following table :—

Rainfall in Inches at Oxford, Month by Month, during the Year 1897.

	Actual fall.	Mean of 30 years.	Difference from the mean.	
January ..	1·85	2·16	−0·31	—
February ..	2·41	1·76	—	+0·65
March ..	2·61	1·50	—	+1·11
April	1·95	1·66	—	+0·29
May	0·85	1·83	−0·98	—
June	1·70	2·68	−0·98	—
July	2·57	2·63	−0·06	—
August ..	3·94	2·32	—	+1·62
September ..	2·25	2·75	−0·50	—
October ..	1·32	2·75	−1·43	—
November ..	1·15	2·10	−0·95	—
December ..	2·50	2·10	—	+0·40
	25·10	26·24	−5·21	+4·07

It will be seen from this table that there has been a total deficit for the year of 1·14 inches.

Our bacteriological examinations of 248 samples have given the following results; we have also examined 41 other samples, from special wells, stand-pipes, &c., making a total of 289 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	805
New River, filtered (mean of 25 samples) ..	21
Thames, unfiltered (mean of 25 samples) ..	15,369
Thames water, from the clear water wells of five Thames-derived supplies (mean of 123 samples)	45
Ditto ditto .. .. highest	372
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	1268
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	22

Table showing the Average Monthly Bacterial Variations during the Year.

Month.	Thames, unfiltered.	Five Thames-derived Companies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London), filtered.	
January	6409	30	1420	37	1460	20	
February	9580	22	1589	20	1177	40	
March..	9187	33	1160	30	1080	22	
April	3277	38	892	13	708	27	
May	2937	40	388	44	791	279	
June	73893	74	2005	69	66822	69	
	105253	237	7454	213	72038	457	
	17542	39	1242	35	12006	76	Mean of 1st 6 months.
July	4791	83	754	44	2494	125	
August	4574	51	3420	44	5846	64	
September	98485	72	387	26	3168	36	
October	3547	51	397	35	1588	39	
November	27173	27	488	13	593	12	
December	15396	45	805	21	1268	22	
	153966	329	6251	183	14957	298	
	25661	54	1041	30	2492	49	Mean of 2nd 6 months.
	21601	46	1141	32	7249	62	Mean of 12 months.

The accompanying table shows the average microbic variation for the year of the various London waters. Taken as a whole, it is highly satisfactory as regards the efficiency of combined storage and filtration in producing a water unexceptional for domestic use. On two occasions the bacteriological condition of the water in one of the clear water wells was above the average, the number of microbes rising to double what we regard as a proper, although severe, standard for the water supply of a city like London. This condition was, however, only temporary, and the microbes present were altogether of the harmless river kinds.

It must be kept in mind that we have bacteriologically examined 3249 samples during the past year, instead of only 348 examined in 1896. We now know from day to day the efficiency of each filter in use. The character of the supply of the respective Companies is therefore much more continuously and severely scrutinised than can possibly be the case when bacteriological examinations are taken at intervals of a week or a month. The result of this continuous examination is that we are in a position to immediately inform the Engineers of the Companies of the commencement of any deterioration in the action of the filters.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

NOTICES OF BOOKS.

The Phase Rule. By WILDER D. BANCROFT. Ithaca N.Y.: *The Journal of Physical Chemistry.*

IT is a little difficult to understand why the author has adopted the above title to his work. One's first impression on opening the volume is that Mr. Bancroft has, by dint of much research amongst the published accounts of original chemical work in many lands, evolved a new rule, or improved upon an old one, by which the nature of the pressure-temperature concentration curves of chemical systems could be predicted, together with the critical points on such curves, and that a comparison between various curves as predicted by his (or Gibbs's) rule, and the curves as plotted from the recorded experiments of various observers would be given. Such, however, is not the case.

The phase rule is simply a method of calculating the maximum possible number of branches to pressure-temperature concentration curves of a given chemical system when the total number of chemical compounds or "phases" which can be formed from the elements present is known, due allowance being made for the non-formation of certain compounds in many cases, owing to the presence of antagonistic elements in the system.

Now, since it can only be determined experimentally what compounds can or cannot be formed from a given collection of elements by suitably varying the pressure, or temperature, or concentration, or either or all of the independent variables, and the results of the investigation, when complete, can be plotted at once, and the whole curve with all its branches and critical points displayed; and since the data for calculating the number of branches is not complete until the investigation is far advanced, the "phase rule" appears to be redundant.

There is, however, another standpoint from which the contents of the book may be examined—one which is indicated by the author in the preface, viz., that it is a collection from many sources of all available information about recent research into the pressure-temperature concentration curves of chemical systems, classified according to the nature of the curves and the complexity of the system.

Viewed in this light the work has a distinct value, and we venture to express a hope that the author will from time to time publish supplements to the present volume.

The word "phase" is used as a substantive, and is defined to be "a mass chemically and physically homogeneous," or as "a mass of uniform concentration." Thus ice, water, and vapour are three phases, a solution of a salt, whether dilute or saturated, is a "phase," whilst if the salt begins to crystallise out of the solution there are two "phases," "salt" and "solution."

Chapter III. deals at great length with the pressure-temperature curves of water, sulphur, and phosphorus, these being taken as typical curves for a system of one component, and in this chapter occurs one of the few tentative forecasts that the author ventures upon, viz., that from the direction of the branches representing red phosphorus and vapour, and liquid phosphorus and vapour (page 32) it is just possible that red phosphorus, liquid phosphorus and vapour may co-exist in stable equilibrium at a very high temperature and great pressure, though he gives no idea as to the actual pressure and temperature probably required.

It is a pity the diagrams are not all drawn to scale with the meanings of the various branches attached, as is the case with a few in Chapters V. and VII.; if this were done in future editions the book would be very much easier to read, and it would not be necessary to refer back so often in order to understand the text; in fact a great deal of the text might be very well omitted if the diagrams were perfected.

Fig. 13 on page 79, a concentration temperature curve for H_2O and Fe_2Cl_6, is one of the best in the book, and shows very clearly, without referring to the text, the various changes that take place in a solution of ferric chloride, as the concentration is varied from H_2O at 0° to Fe_2Cl_6 at 100°, beyond which point the curve has not been carried.

Chapters III. to X. deal with the curves for systems with two components only, these can all be clearly shown as plane curves on an ordinary sheet of squared paper.

Chapters XI. to XIX. show the principal types of curves in systems with three components; here, again, the pressure-temperature curves can be plotted without trouble as plane curves, but the concentration curves, "isotherms" and "isobars" require different treatment, and must either be shown as solid curves in three dimensions, or by one or other of the devices due to Schreinemakers, Meyerhoffer, Stokes, Roozeboom, &c.

Roozeboom's, the method adopted by the author, is the most satisfactory hitherto devised, though it requires a different diagram for every pressure to show a complete set of isothermal curves when the concentration of the system is varied, and is of little use in forecasting results, it is a perfectly clear record of results experimentally obtained, and, like all other curves, is of great use in detecting experimental or clerical errors.

Very few systems with three components have been systematically examined, and none have been exhausted, consequently the isothermal curves in this section of the book are generally largely guesswork sketches, whilst the author makes no reference to the companion series of isobars on a concentration-pressure diagram.

The first nineteen chapters, besides the curves which have been selected as types for illustration, contain numerous tables from which the corresponding curves for other systems may be wholly or partially plotted. A critical examination of these shows us what a large field yet lies open to original research.

Chapter XX. deals with systems of four components, limited by the proviso that one of the four is water, because no others have yet been examined.

In this class the curves would have to be so specialised and multiplied that the author has wisely made no attempt to show any, and relies altogether upon the old-fashioned tables of figures, which after all can, with time and patience, be made to yield a great deal more information than is visible on the surface.

The amount of labour bestowed on this work by the author may be gauged by the fact that the published works (in nearly every European language) of no less than 200 writers have been consulted, and full references given for the benefit of those who may wish to consult the originals.

CORRESPONDENCE.

MOLECULES AND LIQUEFACTION HEATS.

To the Editor of the Chemical News.

Sir,—The letter from Mr. P. J. Beveridge appearing in the Chemical News (vol. lxxvi., p. 264) is of interest as giving a theoretical basis to one of the relations discussed by me (Chemical News, vol. lxxvi., p. 234). Expressed symbolically, the relation obtained by Mr. Beveridge on *à priori* reasoning is $\frac{3\,T}{M\,L}$ = constant; T being the absolute temperature of fusion, M the molecular weight, and L the heat of liquefaction per unit mass. Substituting $\frac{6{\cdot}4}{S}$ (S = specific heat) for M, the relation $T\,S = 2{\cdot}1\,L$ at once obtains; this is the relation proposed in different forms by Dr. Richards, Mr. Crompton and myself, and by me restricted as holding only between elements closely related to each other. The value of the ratio between the heat of liquefaction and the total heat at the melting point obtained above is of the same order, but smaller than the empirically derived numbers given by me; the reason of this is supplied by Mr. Beveridge's argument introducing the polymerisation of the molecule in the liquid state.—I am, &c.,

Noel Deerr.

Windsor Forest, West Coast, Demerara.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxv., No. 23, December 13, 1897.

The Minister of Public Instruction communicated the approval of the President of the Republic of the election of M. Ditte as a member of the Chemical Section, in the place of the late Prof. Schützenberger.

New Method for the Attack of Platinum. Preparation of Bromoplatinate of Ammonium and of Potassium.—Georges Méker.—Already inserted.

Phosphorous Oxide.—A Besson.—Already inserted.

Properties of Carbide of Sodium.— Camille Matignon.—Carbide of sodium is obtained in the form of a white powder; its density at 15° is 1·575, and it appears to be quite insoluble. Dry air and oxygen have no effect on it at ordinary temperatures, but on gently heating combustion takes place, leaving a residue of Co_2Na_2. In the presence of chlorine gas it becomes incandescent, and with bromine the reaction is of almost explosive violence. Iodine has a more moderate action, and C_2I_4, melting at 185°, can be obtained. Hydrogen has no action at all. When thrown into water, carbide of sodium explodes violently, giving a deposit of carbon. It also becomes incandescent when in contact with CO_2 and SO_2. It acts in the cold on a large number of organic substances. The primary and secondary alcohols give off acetylene, giving rise at the same time to the corresponding alcoholate $2C_3H_7OH+C_2Na_2=C_2H_2+2C_3H_7ONa$.

Series of New Cyclic Ketones.—A. Behal.—These ketones are obtained from the heavy oils distilled from Stockholm tar, by first treating them with alkalis; this removes the acids, phenols, &c. The supernatant oil, after washing with distilled water, is shaken up with hydrochloric acid, in proportions variable according to experience, until when diluted and neutralised with carbonate of soda, none remains unacted upon. This solution is treated with a current of steam, and the water being distilled off, leaves an oily layer which is decanted. After repeating this operation once or twice, a slightly yellow liquid, smelling of menthol, remains. The ketones are separated from this liquid by means of hydrochloric acid of variable strengths. To obtain the ketones in a state of purity, they are transformed into oximes by means of hydrochlorate of hydroxylamine and oxide of zinc, in alcoholic solution. The benzoyle derivative is separated in the solid state by treating the oxime with chloride of benzole in the cold. When the

benzoyles are treated in alcoholic solution with an excess of soda, the oximes are easily regenerated in a state of great purity. The oxime fusible at 102° furnishes a ketone boiling at 192°; it is soluble in water, and its density at 0° is 0·9539. These ketones are very numerous, and belong for the most part to the series of benzenic tetrahydrides, which are at present very little known.

Neutralisation of Glycero-phosphoric Acid by the Alkalis in the presence of Heliantine A and Phenolphthalein.—H. Imbert and A. Anstruc.—Experiments have shown that, contrary to expectation, glycero-phosphoric acid does not act on heliantine A and phenolphthalein in the same manner as phosphoric acid. It first behaves as an acid, but if a sufficient quantity of soda be added to render it neutral to heliantine, it still remains acid to phthalein.

Heat of Neutralisation of Glycero-phosphoric Acid.—H. Imbert and G. Belugou.—The authors give a table showing the heat of neutralisation of glycero-phosphoric acid, with both soda and potash, from which it appears that the first molecule of the alkali gives off as much heat as when acting on free phosphoric acid; the second molecule gives off considerably less heat, while the action of the third molecule is *nil*.

No. 25, December 20, 1897.

The Permanent Secretary announced the loss the Academy has sustained by the death of M. Brioschi, of Milan.

Duration of the Phosphorescent Power of Sulphide of Strontium.—Jose Rodriguez Mourello.—Five tubes containing sulphide of strontium, prepared either—A, by reducing sulphate of strontium with carbon; B, from carbonate of strontium and sulphur; C, by the action of sulphuric acid and strontia; D, by M. Verneuil's method; and E, by M. Verneuil's method modified by the author (M. Mourello). They were first kept in the dark for three days, so as to entirely lose all phosphorescence; then, after being simultaneously exposed to light for 15 minutes, they were again taken into the dark, and the relative brightness of each was in accordance with the order in which they are here mentioned, A, B, C, D, E. After an hour, A was much less bright, B had lost a little in intensity, but C D and E showed no change; fifteen minutes later C began to show a difference, followed shortly afterwards by D, while E remained still without any apparent change. A and B had lost all their phosphoresence three hours later, C after five hours, and D after six hours, whilst E still retained some phosphoresence after 12 hours, though only to a very small extent.

Volumetric Estimation of Antimony.—H. Causse.—The author describes a new method for the volumetric estimation of antimony, which is based on the fact that when antimonious acid, either free or combined, comes into the presence of iodic acid, this latter is destroyed, and the antimonious acid passes integrally to the state of antimonic acid, while a quantity of iodine proportional to the amount of the iodic acid decomposed is set at liberty, $5Sb_2O_3+2IO_5=5Sb_2O_5+2I_2$

On Cerium.—M. Boudouard.—(See p. 27).

Action of Piperidine on the Carbonic Ethers from the Phenols; Formation of Aromatic Urethanes.—MM. Cazeneuve and Moreau.—Piperidine, unlike the primary aromatic amines, does not give a symmetrical ureate, but always a urethane, according to the following equation :—

$$C_5H_{11}N+CO\lessgtr^{OR}_{OR}=CO\lessgtr^{NC_5H_{10}}_{OR}+R.OH.$$

R being an aromatic radical. This reaction recalls the action of a molecule of ammonia on carbonate of ethyl, but with piperidine the reaction is limited to a urethane. Three hitherto unknown urethanes are described, viz., phenylic, gaiacolic, and naphtholic B urethanes from piperidine.

MEETINGS FOR THE WEEK.

MONDAY, 24th.—Society of Arts, 8. "Decorative Bookbinding," by Cyril Davenport.
TUESDAY, 25th.—Society of Arts, 8. "Renaissance Woodwork in England," By J. Hungerford Pollen.
—— Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LLD., F.R.S.
WEDNESDAY, 26th.—Society of Arts, 8. "Fireproof Construction of Domestic Buildings," by Thomas Potter.
THURSDAY, 27th.—Royal Institution, 3. "The Halogen Group of Elements," by Prof. Dewar, M.A., LL.D.
FRIDAY, 28th.—Royal Institution, 9. "Instinct and Intelligence in Animals," by Prof. C. Lloyd Morgan, F.G.S.
SATURDAY, 29th.—Royal Institution, 3. "Cyprus," by Prof. Patrick Geddes, F.R.S.E.

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THE CHEMICAL NEWS.

VOL. LXXVII., No. 1992.

A NOTE ON

SOME FURTHER DETERMINATIONS OF THE DIELECTRIC CONSTANTS OF ORGANIC BODIES AND ELECTROLYTES AT VERY LOW TEMPERATURES.*

By JAMES DEWAR, M.A., LL.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution,
and
J. A. FLEMING, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London.

(Concluded from p. 27).

SUBSEQUENTLY to the completion of the experiments described in this paper the suggestion has been made by R. Abegg (*Wied. Ann.*, lxii., p. 249) that the high dielectric values at low temperatures are due to polarisation of the electrodes of the condenser, and that the capacity measured is a polarisation capacity and not a true dielectric capacity, and he supports this contention by pointing out that whenever we have obtained a large dielectric value at the low temperature it has always been measured with an electromotive force of 1·434 volts, which is less than the ordinary full reverse electromotive force of polarisation.

There are, however, reasons for considering that this contention is not a valid one. In the first place, we have always in all the measurements begun operations by testnig the dielectric capacity of our condenser with an electromotive force of one Clark cell (=1·434 volts) in order to see roughly whether the dielectric value was large or small. If it was a small value we then gradually increased the electromotive force until a good readable galvanometer deflection was obtained. We never found that, with an electromotive force of 1·434 volts, the dielectric constant of any substance was greater than with a much higher voltage.

In the next place, in many cases we changed from a working electromotive force of about 20 volts to one of 1·434 volts, and we never found any marked discontinuity in the calculated value of the dielectric constant at that point. If our previous papers on this subject are examined the following instances may be found.

TABLE VII.—*Measurement of various Dielectric Constants with different Electromotive Forces.*

Substance.	Temperature.	Dielectric constant.	Voltage with which constant was measured.	Reference.
Ice	− 89·4	27·6	19·8	*Roy. Soc. Pr.*, lxi., p. 318.
	− 87·2	29·0	1·4	
„	−124·2	18·1	20·3	*Ibid.*, p. 321.
	−119·2	21·8	1·4	
Sodic chloride, 10 p.c. solution ..	−118·5	21·2	20·2	*Ibid.*, p. 307.
	−114·0	22·3	1·4	
Potassic chromate, 30 p.c. solution ..	−112·4	16·9	20·0	*Ibid.*, p. 387.
	−100·0	22·3	1·4	
Cupric carbonate, 10 p.c. suspension	−124·7	16·5	18·2	*Ibid.*, p. 390.
	−120·8	21·8	1·4	
Baric hydrate, 5 p.c. suspension	−178·0	23·9	19·5	*Ibid.*, p. 372.
	−174·2	25·5	1·4	
Bismuth oxide, 10 p.c. suspension	−129·2	19·9	17·8	*Ibid.*, p. 376.
	−127·3	24·5	1·4	

* A Paper read before the Royal Society, December 9th, 1897.

An examination of the above instances will show that if the electromotive force is changed from about 20 volts to 1·4 volts, it does not make a greater difference in dielelectric constant than can be properly ascribed to the accompanying change in temperature.

[Again the following measurements were made at about the same voltage:—

Substance.	Temperature.	Dielectric constant.	Charging voltage.
Potassic bicarbonate ..	−166·5	2·80	19·8
Sodic bicarbonate.. ..	−166·7	48·70	19·8
Ferric chloride	−133·8	4·23	19·8
Sodic chloride	−129·2	14·55	20·2
Cupric carbonate	−132·7	3·42	18·2
Cupric sulphate	−133·2	16·40	19·7
Lithic hydrate	−198·0	3·23	19·8
Baric hydrate	−196 8	20·10	19·5

It is unlikely that polarisation accounts for the differences between the dielectric constants of the above substances taken, pair and pair, when measured at nearly identical temperatures, and very nearly the same voltages. —*November* 8, 1897].

In order to settle the matter finally we propose, however, to re-measure a number of those substances which have shown high dielectric values at the low temperature when measured by the galvanometric method at a frequency of 120, but using in all cases an electromotive force of 100 volts.

If under the larger electromotive force the dielectric values of some electrolytes still remain large, it will be difficult to ascribe this large value to polarisation.

The facts, however, admit of another interpretation. It is clear that the dielectric constants of some substances at low temperatures are vastly more susceptible to change of electromotive force frequency than is the case with others, and that the electric strain produced by a given electric stress varies in some cases enormously with the time of imposition of the stress but very little in others.

Another argument against the view that these high dielectric values are due to polarisation, as ordinarily understood, is as follows:—The results of most numerous experiments on water show that the dielectric constant at or near 0° C. is a number not far from 80. This value is obtained whether the electromotive force reversals are infinitely slow or whether they are very large. The results of the measurement of the electrical refractive index of water even with ether waves only 4 m.m. in length, and, therefore, having a frequency of about $7{\cdot}5 \times 10^{10}$, as given recently by Lampa (*Wien. Ber.*, Part 2*a*, p. 587, 1896; also p, 1049, 1897), indicate a number not far from 9·5 as the refractive index, and hence give a dielectric value of 90. There can be no question of polarisation of electrodes in this last case. On the other hand, an increase in frequency which hardly affects the value of the dielectric constant of water is sufficient to greatly decrease that of ethylic alcohol, and at the same frequency the dielectric constant of ethylic alcohol was found by Lampa to have fallen to a value of 5. Hence ethylic alcohol is more sensitive to change of frequency than water. There is, therefore, no *à priori* reason why we might not expect to find the same thing even in a much greater degree in certain other bodies at lower temperatures, viz., a true high dielectric value for a certain frequency, but great sensitiveness to increse of frequency in such fashion that increase of frequency greatly reduces the dielectric value. At the present stage of the enqniry it seems undesirable to endeavour to regard the facts wholly from the point of view of one hypothesis as to the nature of electrolysis.

We have again to mention with pleasure the assistance we continue to receive from Mr. J. E. Petavel in the observational part of these investigations.

Note added December 8, 1897.—Since the above paper was printed we have repeated some of our former experi-

ments with the 5 per cent solution of rubidic hydrate and the 5 per cent solution of potassic hydrate, using the original method in which a condenser having the frozen electrolyte as dielectric is charged and discharged through a galvanometer, but employing much higher charging voltages. The object of these experiments was to apply a further test of the validity of the contention put forward by R. Abegg, that we have obtained high dielectric values for certain of these frozen electrolytes in consequence of having invariably used an electromotive force of 1·434 volts in the experiments with these particular substances. In order to be able to work with larger electromotive forces we arranged three galvanometers of the Holden d'Arsonval type otherwise exactly similar, except in having different sensibilities and resistances. One was the 500-ohm galvanometer used in all our previous condenser experiments, another was a 100-ohm coil galvanometer, and a third was a 4-ohm coil galvanometer. These were used at the same distance (125 c.m.) from the scale as formerly. An approximate test for the relative sensibility of these galvanometers was made by placing a Clark standard cell in series with each galvanometer through 100,000 ohms and noting the scale deflection produced. As the internal resistance of the galvanometers was at most only ½ per cent of the total resistance, these scale deflections may be considered to be approximately produced by the same current. The scale deflections in centimetres were—

For the 500-ohm galvanometer..	37·3	c.m.
„ 100-ohm „ ..	6·7	„
„ 4-ohm „ ..	0·55	„

Hence the sensibilities are in the ratios of these deflections, and the deflections of the 100-ohm galvanometer must be multiplied by 5·5, and those of the 4-ohm galvanometer by 67·8, to reduce their scale readings to equivalent deflections in terms of the 500-ohm galvanometer.

The 500-ohm galvanometer was then used with the condenser and vibrator, as described in one of our previous papers (*Roy. Soc. Proc.*, lxi., p. 300, 1897). The condenser having gaseous air as dielectric, the scale deflection for a frequency of 120 and an electromotive force of 97 volts was 3·2 c.m. when corrected for capacity of leads.

The condenser then had its dielectric space filled with the 5 per cent solution of rubidic hydrate, and was frozen in liquid air. The dielectric constant was next measured, using an electromotive force of 17·8 volts and the 500-ohm galvanometer. The value of the dielectric constant found, when corrected for the capacity of the leads, was 65·6. The mean corrected scale deflection was 38·5 c.m. for 17·8 volts. This, reduced to its equivalent for 97 volts, is 210 c.m. and $210/3·2 = 65·6$.

In the next place, the same experiment was repeated employing the 100-ohm galvanometer and an electromotive force of 79 volts. Applying the necessary corrections to the observed scale deflection of 23·5 c.m., and reducing to the equivalent deflection on the 500-ohm galvanometer gave 160 c.m. as the value of the reduced deflection. Hence $160/3·2 = 50$ is the dielectric constant. The rather considerable difference between these values (65·6 and 50) is not a matter for surprise, having regard to the extreme steepness of the dielectric curve of the rubidic hydrate solution at about the temperature of liquid air. As we were merely desirous of determining whether a considerable increase of electromotive force would greatly diminish the large dielectric value, we did not trouble to put in operation the rather elaborate platinum thermometer arrangements for determining the exact temperature of the dielectric. A reference to the dielectric-temperature curve of rubidium hydrate (*Ibid.*, p. 378) will show that even one or two degrees of temperature change in the neighbourhood of −185° C., or −200° pt. makes a very considerable alteration in the dielectric value. The result, however, ascertained is that changing the electromotive force from 1·434 volts to 17·8 or 79 volts does not bring down the dielectric constant from a large value to a small one.

In the same way the 5 per cent solution of potassic hydrate was tested.

Using the 500-ohm galvanometer and an electromotive force of 9·88 volts we found 153 as the dielectric constant of the frozen electrolyte at the temperature of liquid air. Employing the 4-ohm galvanometer and 79·5 volts we found 175 as the dielectric constant.

All the above observations were taken at the temperature of liquid air and with an electromotive force frequency of 120. It is, therefore, quite clear that as far as these two frozen electrolytes are concerned, raising the charging voltage to a value far above that of the average electromotive force of polarisation does not bring down these abnormal values of the dielectric constant. On the other hand, a relatively small decrease in the temperature or *increase in the frequency at low temperatures* suffices to reduce the dielectric value of these frozen hydrates very considerably.* We may, therefore, say that the contention put forward by R. Abegg that the high dielectric values we have found for certain substances at the liquid air temperature are really polarisation capacities, does not seem to be borne out by the results of further experiment, and for the following reasons:—

i. Because a very great increase in the charging electromotive force does not in any corresponding degree reduce the abnormally high dielectric values of certain frozen electrolytes to much smaller values.

ii. Because when, in the course of observations to construct a temperature dielectric curve, the working electromotive force has been changed from a value below the counter-electromotive force of polarisation to a value far above it, there is no break or discontinuity in the curve of dielectric value.

iii. Because the great difference between quite similar electrolytes, such as the 10 per cent solution of potassic and sodic carbonates, in respect of dielectric constant at equally low temperatures and under equal charging electromotive forces, is left unexplained.

iv. Because in the case of many substances, such as frozen ammonic hydrate, ice, and oxide of copper in suspension in ice, at very low temperatures, we find high dielectric values, even though employing alternating currents of fairly high frequency (350 ∽).

v. Because the high dielectric value of water and alcohol and other bodies at ordinary temperatures remain, even when the observations are taken, with alternating electromotive forces of exceedingly high frequency and under conditions when there are no electrodes to polarise, as when the electric refractive index is measured with electromagnetic radiation.

We consider that the results of observations so far made are best expressed by merely considering the dielectric constant to be a function of the frequency and the temperature, and represented therefore by a *dielectric surface*, which surface has for some substances a region of abnormal dielectric ordinate.

In all cases so far examined by us, lowering the temperature sufficiently acts in the same manner in reducing the dielectric constant as sufficiently increasing the frequency, and both actions reduce the abnormally large dielectric values of some substances to values more approximately equal to the square of the optical refractive index of the body.

* The effect of increased frequency of electromotive force reversals in decreasing the dielectric constant is evidently dependent upon the temperature as well as on the physical state of the body. In the case of water an increase in the frequency from zero to 10^6 hardly affects the dielectric constant at all. In the case of ice at 0° C. the same increase in frequency reduces the dielectric constant from 80 to between 2 and 3. In the case of ice at −50° C., as we have shown above, an increase in frequency from 120 to 350 reduces the dielectric constant from about 60 to about 3·6. (December 21, 1897).—A. W. R

The question then to be considered is the physical reason for the high dielectric values for particular substances for certain ranges of electromotive force, frequency, and temperature. Whether this abnormal electric displacement is considered to be the result of a molecular strain superimposed on a true electric strain, or whether it is the beginnings of that molecular deformation which finally ends in chemical decomposition, remains to be seen. Having regard to the enormously high electrical resistivity which we have shown these frozen dielectrics to possess, it does not appear to us likely that polarisation in the sense of a deposition of ions on the electrodes can be invoked to explain the differences we have shown exist.

SCORIFICATION *VERSUS* CUPELLATION.

An Improved Method for Laboratory Purposes.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

In order to carry out a successful cupellation by the aid of the well-known muffle furnace, especially when results of great accuracy are sought for, many various precautions have to be considered, both as regards the careful regulation of temperature and also with respect to the amount of air admitted into the furnace, so as to continuously produce a superficial oxidation of the lead to litharge, as fast as absorbed by the bone-ash comprising the cupel. On the other hand, scorification of a regulus produced from the smelting of argentiferous lead is often resorted to prior to cupellation of the same, in order to reduce in bulk the original matrix, and by so doing at least partially avoid the more tedious operation of cupellation. Again, the addition of alkaline nitrates is frequently adopted in order to provide a quick oxidant prior to cupellation, although in most cases affording inaccurate results. In order, therefore, to obviate these difficulties, the author has for some time past employed both strontium and barium sulphate as a substitute for bone-ash, at the same time avoiding entirely the tedious process of cupellation; and, by so doing, arrives at more accurate results in a very short space of time. The process is conducted in the simplest manner possible by the introduction into an ordinary clay roasting-dish of convenient dimensions of a sufficiency of barium sulphate; a small bed being sunk into the centre of the same by gently compressing the powder by the aid of a smooth pestle.

The cavity thus formed is now quickly raised to a dull red heat by means of an ordinary blowpipe attached to a foot bellows. The alloy is next dropped in, to which is immediately added the same bulk of a further alloy, consisting of lead in admixture with 10 per cent of bismuth. The flame from the blowpipe is now allowed to impinge upon the melt until it assumes a bright red tint; the flame is then shortened and raised to within half an inch of the same, and a full blast of air maintained. The regulus at once assumes a spherical condition and commences to rotate rapidly, at the same time disappearing with remarkable rapidity. About one-quarter of the litharge thus oxidised is absorbed by means of the sulphate, the remainder solidifying around the lead.

In cases where large quantities are employed, the operation should be stopped at intervals, and the halo thus formed removed by a spatula; the scorification is then continued until pure silver remains.

The speed with which the lead is thus oxidised and removed by means of the bismuth alloy is most remarkable. By means of a barytes bed only 6 inches in diameter I have frequently removed as much as 2 lbs. of lead in less than an hour. The facility also of obtaining the sulphate in most laboratories where estimations of sulphur are carried out will be easily recognised. If a sufficiency, however, cannot be thus obtained, the commercial ground mineral (which answers the purpose admirably) can always be relied upon in any quantity and at a very low rate.

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PERSULPHURIC ACID AND ITS SALTS.

By M. ELBS.

It is hardly necessary to recall the fact that persulphuric acid was obtained for the first time by Berthelot in 1881, by the electrolysis of ordinary sulphuric acid. The properties of this acid have been since studied by Richarz (in 1888), and again in 1891 by Marshal, who also described some of its salts.

Since 1893 the work done on this acid has considerably increased, and it seems to me to be of some value to give a review of what has been done.

Aqueous sulphuric acid is a conductor of electricity; and, further, a conductor of the second class, since, while allowing the current to pass, it becomes decomposed, giving two distinct products at the two poles. Its electrical dissociation furnishes theoretically hydrogen and an acid remainder. But as sulphuric acid, in its quality of a bibasic acid, contains in its molecule two atoms of hydrogen, its dissociation can be effected in two distinct manners:—

I. *In a Complete Manner.*—Each molecule of H_2SO_4 gives two ions ($\overset{+}{H}$) and one bivalent ion ($\overset{-}{SO_4}$) according to the equation $H_2SO_4 = 2(\overset{+}{H}) + (\overset{-}{SO_4})$. Very dilute solutions of sulphuric acid behave in this manner. But, as a matter of fact, by electrolysis they always give off a gas, $H_2 + O$. The remainder ($\overset{-}{SO_4}$) goes to the positive pole, and reacts on the water according to the equation $SO_4 + H_2O = H_2SO_4 + O$, while at the negative pole we obtain the two corresponding atoms of hydrogen; or, to be more precise, the sulphuric acid always remains as sulphuric acid, and it is the water only which is dissociated into its elements H_2 and O.

II. *In an Incomplete Manner.*—A more concentrated sulphuric acid (D = 1·4) gives by electrolysis the ions $\overset{+}{H}$ and $\overset{-}{HSO_4}$. The ions ($\overset{-}{HSO_4}$) go to the positive electrode and combine mutually, at any rate to a great extent, and form persulphuric acid:—

$$2O_2S\langle^{O-}_{OH+} = O_2S\langle^{O\text{——}O}_{OH\ OH}\rangle SO_2.$$

As a secondary reaction these same ions may react to a small extent on the water of the electrolyte, and re-form sulphuric acid with liberation of free oxygen:—

$$2O_2S\langle^{O-}_{OH} + H_2O = 2O_2S\langle^{OH}_{OH} + O.$$

At the negative pole two atoms of hydrogen are given off. According to these reactions, dilute solutions of sulphuric acid (density lower than 1·2) will not give any persulphuric acid at all, while solutions of medium concentration (densities from 1·3 to 1·5) of which the ions may be represented by ($\overset{+}{H}$) and ($\overset{-}{HSO_4}$), will in almost every case give persulphuric acid. And, in the latter case, the proportion may reach 70 per cent of the theoretical amount. For higher concentration the return diminishes. Firstly, because the concentrated sulphuric acid may partially decompose the persulphuric acid, and secondly, because the latter is a bad conductor of electricity. In contact with the negative pole, persulphuric acid should be decomposed by the hydrogen which is disengaged:—

$$OS_2<^{O\text{——}O}_{OH\ HO}>SO_2+2H=2O_2S<^{OH}_{OH}.$$

It therefore becomes necessary, in order to obtain good results, to separate the liquid round the anode from that round the cathode by means of a porous pot.

Free persulphuric acid is very unstable in aqueous solution. According to the conditions, it will decompose into sulphuric acid and peroxide of hydrogen, or sulphuric acid and oxygen. These two forms of decomposition may be represented by the following equations:—

I. $H_2O_2O_8+2H_2O=2H_2SO_4+H_2O_2$.

II. $H_2S_2O_8+H_2O=2H_2SO_4+O$.

When warm the decomposition takes place only according to the second equation.

The principal reactions of persulphuric acid are as follows:—

1. Disengagement of oxygen by heat.
2. Decolouration of indigo.
3. Decomposition of hydrochloric acid or chloride of sodium, with the production of chlorine, and the analogous reaction with bromide and iodide of potassium.

Among the salts of persulphuric acid, the best known is the persulphate of ammonium, which can be prepared by the electrolysis of a saturated solution of sulphate of ammonia. The reactions are as follows:—

$$1.\ (NH_4)_2SO_4=\overset{+}{(NH_4)}+\overset{-}{(NH_4SO_4)}.$$

$$2.\ 2\overset{-}{(NH_4SO_4)}=(NH_4)2S_2O_8.$$

Persulphate of ammonium takes the form of white crystals. It is stable when in the dry state, and up to the temperature of 100° C., but, on the other hand, it decomposes when moist, even at the ordinary temperature, with the production of strongly ozonised oxygen:—

$$(NH_4)2S_2O_8+H_2O=2NH_4HSO_4+O.$$

Two parts of cold water dissolve one part of persulphate of ammonium. Persulphate of ammonium gives the same reactions as persulphuric acid, besides some others, as follows:—

1. When warmed with a solution of sulphate of aniline, it gives aniline black.
2. A solution of fuchsine with acetate of soda is decolourised by persulphate of ammonium.
3. With a solution of manganous sulphate, persulphate of ammonium gives a precipitate of binoxide of manganese. This reaction is expressed by the following equation:—

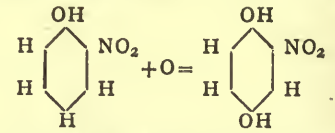
$$MnSO_4+(NH_4)_2S_2O_8+2H_2O=$$
$$=MnO_2+H_2SO_4+2NH_4HSO_4.$$

4. With a solution of carbonate of potassium, persulphate of ammonium gives a very dense, crystalline precipitate of persulphate of potassium. No salt of persulphuric acid is insoluble. Persulphate of potassium is only difficultly soluble, but all other persulphates dissolve easily.

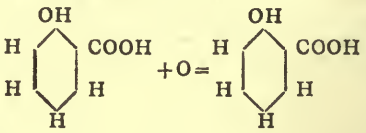
The slight solubility of persulphate of potassium enables one easily to prepare this salt by the electrolysis of a cold saturated solution of sulphate of potassium in sulphuric acid of 1·3 density. Under these conditions, and using a current of about three ampères, we can rapidly obtain a crystalline deposit of persulphate of potassium.

The metallic sulphates, treated under the same conditions, behave in a very variable manner. Those which give the best return in persulphate are those of ammonium, potassium, and aluminium. Persulphate of ammonium only, up to the present, seems destined to be of any industrial use. Its use as a bleaching agent is already under consideration, and it is already being used for the purpose of introducing directly the hydroxyl group into the benzinic nucleus.

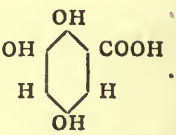
Thus ortho-nitrophenol in alkaline solution, treated with persulphate of ammonium, becomes oxidised and produces nitro-hydroquinone:—



In an analogous manner salicylic acid would be transformed into hydroquinone, carbonic acid, or into pyrocatechine carbonic acid (Schering).



or else—



In the same manner we can transform oxyanthroquinone into alizarine, alizarine into purpurine, Bordeaux alizarine, or alizarine cyanine. Persulphate of ammonium is also used, concurrently with cyanide of potassium, for the extraction of gold. The ordinary reaction in the presence of air is as follows:—

$$4KCN+2Au+H_2O+O=2KAu(CN)_2+2KOH.$$

Oxidation is much more rapid when we make use of persulphate of ammonium—

$$4KCN+2Au+(NH_4)_2S_2O_8=$$
$$=2KAu(CN)_2+(NH_4)_2SO_4+K_2SO_4.$$

It seems very probable that the applications of persulphate of ammonium will become more and more numerous, the more so as the cost of its manufacture is low. But at the same time it must not be forgotten that as an oxidising agent it is inferior to many other substances in common use. Its decomposition only furnishes one molecule of free oxygen, while bichromate of potassium, for example, gives three.— *Zeitschrift für Angewandte Chemie*, p. 195, 1897.

ON THE REACTIONS BETWEEN MERCURY AND CONCENTRATED SULPHURIC ACID.

By CHARLES BASKERVILLE and F. W. MILLER.

Many text-books class the reactions between copper and concentrated sulphuric acid along with mercury and sulphuric acid, stating merely that a sulphate of copper or mercury is formed with the evolution of sulphur doxide.

In other communications (*Jour. Am. Chem. Soc.*, xvii., 904, and xviii., 942), one of us (Baskerville) has shown that while the formula—

$$Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O,$$

expresses in fact the main reaction when these two substances are brought together, even at different temperatures, that only at 270° C., or higher, is that reaction unaccompanied with very important and complex secondary reactions. In preparing sulphur dioxide, by heating together copper and concentrated sulphuric acid, invariably a black or brown material discolours the colourless acid. This dark substance is, in the main, cuprous sulphide.

Not finding the reaction between mercury and concentrated sulphuric acid worked out in detail in any of the literature at our command, and since so much wrong data have been recorded concerning copper under similar conditions, it was deemed advisable to study this reaction at different temperatures,

The reaction is by no means like that of copper. The primary reaction depends upon the preponderance of mercury or acid, the temperature, and the time during which it is allowed to continue.

If the mercury be in larger amounts than the acid, invariably almost pure mercurous sulphate is produced:—

$$2Hg+2H_2SO_4=Hg_2SO_4+SO_2+2H_2O.$$

It will be well to state here that the mercurous sulphate so produced is a white crystalline substance and not black, as stated in Roscoe and Schorlemmer's "Treatise on Chemistry" (vol. ii., Part i., p. 401).

Series of experiments in duplicate were carried out at different temperatures when the acid was in large excess. A qualitative experiment showed that mercury decomposed concentrated sulphuric acid at the ordinary atmospheric temperature, about 20° C. This experience is contrary to that stated in a number of text-books. Experiments carried out at 100° C. upon a water-bath, lasting during twenty hours, in apparatus especially arranged to insure only the presence of dust-free, dry air showed that about one-fifth of the mercury had entered into the reaction. Ten grms. of the mercury and from 50 to 100 grms. acid were used. Expecting the results to exhibit this reaction:—

$$Hg+2H_2SO_4=HgSO_4+SO_2+2H_2O,$$

we were surprised to find so much less sulphur dioxide evolved than should have been. The crystalline sulphate produced gave 20·75 per cent SO_4, which is very near 19·35 calculated for mercurous sulphate. Again, at 150° C., when the flask containing the mercury and acid was kept at a practically constant temperature by being immersed in a sulphuric acid bath for two hours, the amount of sulphur dioxide evolved was much below the theoretical. At least half of the mercury in each of these experiments was dissolved. The white crystalline layer of sulphate which separated out as the amount of metallic mercury decreased was augmented by another layer, which had been in solution, when the acid became cool. Both were crystalline, but while the latter was powdery, the former was composed of needle-like crystals. To avoid the formation of the basic sulphate, $HgSO_4.2HgO$, which was always produced in our efforts to wash out the remaining acid with water, we used ninety-five per cent alcohol. Four washings were sufficient; in fact, on further washing even with alcohol, some basic sulphate was formed. On analysis of this alcohol-washed substance, which had been dried to a constant weight at 100° C., we obtained:—

	Calculated for $Hg_3(SO_4)_2$, or $Hg_2SO_4.HgSO_4$.	Found.
SO_4	24·24	23·96 24·27
Mercury (-ous).. ..	50·38	50·27

At 200° C. the percentage of mercurous mercury dropped to 40; at 250° C. still lower, showing a steady decrease in the amount of mercurous sulphate produced as the temperature increased. When the acid was boiled and the mercury poured in, the crystalline compound gave 32·91 per cent of sulphur tetroxide when mercuric sulphate contains 32·43 per cent. Evidently some of the acid was not removed by the washing with alcohol.

It was desirable to determine whether the primary reaction took place in steps, *e.g.*, if the metal liberated hydrogen, which in the nascent state attacked the remaining sulphuric acid with the production of sulphur dioxide, such having been recorded by some anthors to be the case in the reactioh between copper and sulphuric acid. Careful experiments at different temperatures, 150° and 200° C., were carried out in an atmosphere of carbon dioxide free from air. One hundred c.c. of the gases given off and collected over a ten per cent solution of sodium hydroxide gave not a trace of hydrogen. The sulphuric acid in this case is evidently reduced directly by the metal. No sulphide was produced, nor any free sulphur.

If portions of the crystalline compound, produced by the treatment of mercury with concentrated sulphuric acid rendered free of acid by washing with alcohol and dried at 100° C., be again treated with acid in similar apparatus, sulphur dioxide is evolved in proportion to the amount of mercurous sulphate there is present. If mercuric sulphate be treated with the acid, no sulphur dioxide is evolved. In fact, if a prepared mixture of mercurous and mercuric sulphates in varying proportions, or any of the crystalline compounds obtained in any of the experiments cited, except that produced by the boiling acid, be treated with fresh acid and heated until the gas evolved ceases to bleach a weak potassium permanganate solution, the crystalline residue then obtained is mercuric sulphate.

Although the relative yield of sulphur dioxide is less, the treatment of mercury with concentrated sulphuric acid has been recommended for class-room experiment on account of neatness and freedom from black residue, which in the case of copper is oftentimes unintelligible to the ordinary student. A slight objection may be urged against this use on account of the volatility of the metallic mercury at the temperature of reaction. Faraday has shown that in spite of its high boiling-point, mercury volatilises at the ordinary temperatures. One of us (Baskerville) has had this fact to contend with in several cases where this method of evolving sulphur dioxide was made use of in quantitative work.

In the experiments given all materials used were pure. The concentrated sulphuric acid was of 1·84 sp. gr. The mercury was purified according to Lothar Meyer's method (*Zeit. Anal. Chem.*, ii., 241), by allowing the distilled metal to flow in a thin stream first through a column of dilute nitric acid, then dilute sulphuric, to dissolve out all lead and tin, finally washed and dried. All apparatus was most carefully cleansed, and when necessary moisture-free and proved to be air-tight.—*Journal of the American Chemical Society*, vol. xix., No. 11.

THE ANALYSIS OF BEARING-METAL ALLOYS, WITH A NEW VOLUMETRIC METHOD FOR DETERMINING COPPER.*

By W. E. GARRIGUES.

Judging by the number of articles that continue to appear from year to year in chemical journals, elaborating more or less complete schemes for the analysis of these alloys, the subject is still a timely one for discussion. There is, furthermore, small likelihood that this apparent interest will lag, in the near future at least, owing to the evident fact—and it is one that must not be lost sight of in passing judgment on the merit of such a combination of methods for separation and determination as the present paper deals with—that we are not considering a material capable of being handled like steel, where accurate methods have been found for ascertaining the quantity of almost every element present, without the necessity of first removing three or four others from solution.

In the light of our present knowledge of the chemical deportment of the metals of the hydrogen sulphide and ammonium sulphide groups, all methods which even approach accuracy must of necessity be comparatively tedious. Not alone is it essential in almost every case to free a solution from interfering elements to reach the one sought, but in very many instances it is all but impossible to get the former out of the way without sustaining loss

* Read before the Chemical Section of the Engineers Society of Western Penns lvania. From the *Journal of the American Chemical Society*, vol. xix., No. 12, December, 1897.

of the latter. Add to this the manipulative difficulties, such as the washing of slimy precipitates that persist in passing the filter medium, and those that in coming down occlude non-volatile salts used as reagents, or sustain loss in ignition through reduction and volatilisation—there is certainly sufficient difficulty remaining to interest many of us for years to come.

The present paper is not written so much with the object of presenting innovations that conduce to speed as to discuss some of the inaccuracies in very commonly used processes, and to considering means for overcoming them, even though at times additional labour may be involved. Of late years the art of successfully working scrap has reached such perfection, that it is probably not an error to assume that the greater part of the metal in alloy bearings, now in use, was at one time doing duty along a varied line reaching from wash-boiler bottoms to tea packages. The inevitable result is that the subject has grown still more intricate, from the analyst's point of view, the range of elements existing in small percentages being greater.

The alloys considered are bronze, brass, and white metal, composed of copper, tin, antimony, lead, zinc, iron, phosphorus, and arsenic.

The advantage of a qualitative analysis, previous to beginning the analysis proper, has often been dwelt upon, and there is but little doubt that it almost invariably repays the trouble tenfold. In the scheme to be outlined here, it is particularly desired to know beforehand whether antimony, iron, zinc, and arsenic are absent; for this purpose we have found the following procedure easy and satisfactory. The sample is oxidised with nitric acid, and evaporated dry, boiled with a little dilute nitric acid, the residue filtered out and washed.

Antimony.—Ignite a portion of the residue intensely, boil with strong hydrochloric acid, and dilute with an equal volume of water. Filter and add considerable water, when a white precipitate indicates antimony. Confirm by orange hydrogen sulphide precipitate.

Arsenic and Iron.—The remaining portion of the residue is warmed with a little caustic soda solution, and dissolved by the further addition of alkali sulphide and heating. The black residue is removed by filtration, and treated for iron by any suitable method. In the alkaline filtrate arsenic is precipitated with ammonia and magnesia mixture, the precipitate filtered out and dissolved in hydrochloric acid, which solution is boiled with sulphurous acid, and then saturated with hydrogen sulphide, when the arsenic, if present, is obtained as sulphide.

Zinc.—The filtrate from the nitric acid insoluble residue is saturated with hydrogen sulphide, the filtrate mixed with one-tenth its volume of strong hydrochloric acid, and potassium ferrocyanide added, when zinc is indicated by a white precipitate of the ferrocyanide.

Quite a large amount of the sample should be used, as otherwise antimony may all pass into the nitric acid filtrate, and thus escape detection. The ignited stannic oxide is entirely insoluble in the boiling hydrochloric acid, while sufficient antimony dissolves to give ample reactions. The large amount of hydrochloric acid is added previous to testing for zinc, to prevent the co-precipitation of any lead that may have escaped coming down as a result of the hydrogen sulphide treatment.

Coming now to the quantitative part of our subject, we have to consider first

The Determination of Single Elements.

Zinc, when present in fairly large quantity, and an absolutely correct determination is not required, can be very conveniently measured by titration with standard potassium ferrocyanide, but in smaller amounts a gravimetric method is preferable. For the details of the process, see Stone (*Journ. American Chem. Soc.*, xvii., p. 413). The end-point is marked by an immediate green colour with cobalt nitrate.

Stone directs that the volume of standard liquor necessary to give the end reaction be determined by a blank experiment, and that this amount be subtracted from each titration. This statement we have been entirely unable to verify, as witness the following set of titrations of varying amounts of the same solution of zinc chloride:—

Zinc chloride. c.c.	Potassium ferrocyanide. c.c.	Total per cent.	Blank per cent.
0	1·5	—	—
5	6·0	30·0	22·5
10	11·8	29·5	25·7
12·5	14·6	29·2	26·2
15	17·5	29·15	26·6
25	29·2	29·2	27·7

Total per cent column is figured on the assumption that the highest titration is per cent zinc, the lower titrations then being multiplied to equal the same volume of zinc chloride used—no blank being subtracted. Figures in blank per cent column are obtained in the same manner, except that the blank is in each case subtracted. It will be noticed that the figures in the latter column are anything but uniform among themselves. To get the best results, the standard solution should be titrated against a known zinc solution of the same strength as the sample under examination. In applying the process absence of copper and iron is essential.

When the conditions of precipitation are fully understood, one of the neatest and most accurate analytical processes is the determination of zinc as phosphate. All metals, inclusive of alkalis, should be absent.

The solution should be exactly neutralised with hydrochloric acid or ammonia, as the case may be, using methyl orange as indicator, unless the liquid contains acetic acid, in which case no further inconvenience results, except that litmus is substituted for methyl orange. A very large excess of ammonium phosphate is to be avoided, as otherwise the precipitate is re-dissolved to some extent. This part of the process is, however, not the delicate matter it might seem from the statement, as will be shown later. The most satisfactory mode of procedure is to add first, say, one grm. of the phosphate, which will not hold up the smallest traces of zinc, and if a large precipitate comes down to continue the addition. Hydrogen sulphide should give no trace of precipitate in the filtrate. It is highly advisable to work only with ammonium salts from the beginning, sodium salts being less good, and potassium salts entirely prohibited, as they are carried down with the precipitate by occlusion in astonishing amounts.

The ammonium phosphate is added to the warm solution of the zinc, which is then further warmed, until the precipitate is entirely free from any flocks, and the solution has completely cleared. Filtering on a Gooch crucible, washing with water and then alcohol, drying at 100° C., and weighing as zinc ammonium phosphate is recommended. Using an ordinary filter paper and igniting seems to cause an unavoidable loss through reduction, no matter what care be exercised in separating the filter. It may, however, be ignited with perfect safety on a Gooch, even though a disc of paper be used as the filtering medium. In the latter case the paper should be turned above the precipitate toward the mouth of the crucible.

The details of the method, with sodium phosphate as precipitant, appear in the last edition of "Crookes's Select Methods." The original author's statement that the ignition gives low results, owing to volatility of the zinc pyrophosphate, cannot be admitted; in fact our excellent results obtained by ignition on a Gooch prove that such is not the case. The same applies to his claim that the precipitation takes place in an acid solution.

Though a difference of opinion as to what constitutes an acid solution may in some cases exist, it certainly does not seem reasonable to apply the term to a liquid smelling strongly of ammonia. The reactions occurring are probably expressed by the equations:—

a. $ZnCl_2+(NH_4)_2HPO_4=ZnHPO_4+2NH_4Cl$.

b. $ZnHPO_4+(NH_4)_2HPO_4=ZnNH_4PO_4+2NH_4H_2PO_4$.

It is even likely that these two stages are entirely separate, since in a cold solution the precipitate is at first as flocculent as an alumina precipitate, while on warming it becomes as dense as barium sulphate. If only the amount of ammonium phosphate called for by the first equation is added, the precipitate remains flocculent, despite continued heating.

The double equation requires nearly five parts ammonium phosphate for one part zinc, and we have successfully thrown down two-tenths grm. zinc with one grm. of the phosphate, obtaining it all as the ammonium salt. The same quantity was also perfectly precipitated with five grms. of ammonium phosphate, but eight grms. left a little zinc in solution. Similarly, 0·008 grm. was completely thrown down with 0·05 and 3·00 grms. respectively, while five grms. caused some re-solution.

Returning to the question of acidity, it will be seen from the equation that monoammonium phosphate remains as a product of the reaction, but the excess of the diammonium phosphate, always used in practice, decomposes on heating to monoammonium phosphate and free ammonia, thus determining the alkalinity of the liquid. The precipitate is soluble with great facility in any kind of acid, or in excess of ammonia. Too much cannot be said in favour of the process for accurate work.

Copper is determined in smaller quantities by the iodide method, and in larger quantities by the new process described below. The latest literature added to the iodide method is Low's paper (*Journ. American Chem. Soc.*, xviii., p. 458). He introduces two modifications: Oxidation of any arsenic present, with potassium chlorate, and neutralisation of the excess of nitric acid with zinc acetate.

There is no doubt, as Low states, that the end point is better, as a result of the use of zinc acetate, than when the sodium salt is employed; the oxidation with chlorate is also a great step in advance for the process. It is, however, a mistake to use any acetate, as the end-point is then at best not clear, though with practice it can be distinguished.

Some time ago the writer had the honour to present to this Section a paper on the iodide method for copper, in which it was proposed to avoid the inaccuracy introduced by the presence of arsenic, by separating the copper from it with glucose in the well-known manner. The object was to retain the clear end-point when the titration is conducted in a very slightly acid sulphuric acid solution. Since that time the following, relative to the subject, has been ascertained:—

When copper and arsenic, either as metals or sulphides, as obtained in the course of analysis, are dissolved in nitric acid, there is very apt to result a solution of the arsenic, both as arsenic and arsenious acid. If now this solution be boiled with chlorate in a fairly concentrated condition, all the arsenic is oxidised to the higher form. Arsenic acid in strongly mineral acid solution, mixed with an iodide, is reduced to arsenious acid with liberation of iodine, causing the result for copper to appear high. In a solution which is, however, only faintly acid from a mineral acid, this reaction does not take place; in fact free iodine will then even oxidise arsenious acid to some extent, but far less so than in acetic solution. In the presence of little acid and arsenious acid, the result for copper would therefore appear low, since the iodine liberated by the copper would be in part consumed by the arsenic, instead of being measured by the titrating liquid. If the copper solution be only faintly acid, and the arsenic all present as arsenic acid, an accurate result for copper is obtained in sulphuric acid solution, and the end point with starch is vastly superior than if either zinc or sodium acetate has been used.

The thiosulphate solution should be standardised on approximately the amount of copper found in the assay, conveniently obtained by measuring out a standard copper sulphate solution, if the best results are to be gotten. In the writer's experience a little more than the theoretical amount of iodine is liberated, and this not in absolutely uniform ratio. For small amounts of copper it is advisable to allow the solution to stand a given time, say ten minutes, between the addition of the iodide and the titration, otherwise the end-point will come and go in a rather unsatisfactory manner.

While the method is good, very much to be preferred to the cyanide titration of Parks and Mohr, after an extended experience with it, we must certainly dissent from Low's claim of superiority for it as against the electrolytic assay.

(To be continued).

NOTICES OF BOOKS.

Notes on Lead and Copper Smelting and Copper Converting. By Hiram W. Hixon. New York and London: The Scientific Publishing Co. 1897. Pp. 116.

In the preface to this excellent work the author informs us that it was not his intention to write a treatise of the subject, but rather to give the benefit of his practical experience to others engaged in similar work: in this we think he has entirely succeeded.

The book is divided into seventeen chapters, and contains twenty-four illustrations, besides eighteen plates.

In Chapter I. the operation of copper matte smelting is gone into in many of its details, both with regard to the charge, the composition of the slag, wind required, &c. With regard to the relative merits of the Roots and the Baker blowers, Mr. Hixon declares entirely in favour of the former, as there is much less leakage from it than from the Baker blower, and the cost of working must necessarily be less.

The first attempt at recovering silver from the dump of accumulated speiss at the Arkansas Valley Works was not a success; the lumps of speiss were too big for the crusher, and considerable damage was done to the machinery; but as the yield of silver was so high, viz., 5 per cent, repairs and improvements were made and the work resumed. Chapter II., in a few sentences, describes the methods in use for extracting gold and silver from matte.

After a chapter on furnace charges, we come to types of furnaces and the differences necessary in them, for the varying quality and kinds of matter to be smelted or roasted. Spouts, settlers, and jackets are discussed in Chap. V., and in the next chapter the methods of blowing-in and barring-down furnaces are given. The handling of blast-furnace slag is always an important point of the management, and the author considers that there are now four methods in use for lead furnaces, and two for copper furnaces, all of which possess great merit. These are considered *seriatim* in Chap. VII.

The next two chapters concern the design of lead blast-furnaces, and the loss attaching to them.

Many improvements in roasting furnaces have been introduced during the past five years, especially with regard to roasting concentrates; the author has designed a roasting furnace that can be coupled direct on to a reverberatory, and the heat from the smelting thus used for roasting, as well as for the conversion of the matte. This is described in Chap. X., with illustrations. In Anaconda the experiment was tried of smelting raw concentrates with hot-blast, but the results were not satisfactory, and, as with copper converting at the same place, it was found that the expense of the linings was too great. Various linings are discussed in Chap. XII., and we next come to the operation of blowing a converter charge; it is a delicate operation, judged to a great extent by the colour of the flame at the nose of the converter, and necessarily demands great skill, only to be obtained by practice. The formation of copper oxide does not occur to any great

extent so long as any iron is present in the matte; but as soon as the iron is all oxidised, and has gone into the slag, the copper commences to oxidise rapidly, and this is the principal thing to guard against.

Chapters XIV. and XV. are devoted to the design and lining of converters; they are in general appearance just like Bessemer steel-converters.

In the Appendix we have specifications of buildings and machinery for copper converter plant, accompanied by some excellent plans and drawing.

The index is good and comprehensive, and the whole printed on very good paper in the usual first-class American style.

Chemistry for Photographers. By Chas. F. Townsend, F.C.S., F.R.P.S. Illustrated, pp. 158. London: Dawbarn and Ward, Lim.

There is perhaps no science which has made such remarkable—and to some extent startling—strides of late years as photography, and for this very reason books of this character are essential. Kodacs, cinematoscopes, and such like, have raised a growing desire among the public to take photographs for themselves; but unforunately they are too prone to go on the "You press the button and we do the rest" principle, and therefore have not much knowledge of what they are really doing.

Photography is largely chemistry, and, as the author points out, "the first essentials to anyone studying chemistry are accuracy and cleanliness." This book differs from most books on the same subject, in that it pays much more attention to the chemical side of the subject than is usual. The reagents used, such as "hypo," silver salts, oxidising and reducing agents, are explained, and their chemical action and formulæ described, apart from the rule-of-thumb photographic use of the reagents. This, however, is not all; we find plenty of purely technical matter, with all the latest methods and improvements in printing, toning, &c.

One of the most valuable parts of this volume is the "Cyclopædic Index," in which not only every article mentioned in the text is indexed alphabetically, but the index is divided into eight columns, setting forth the name, the reference pages, other names, symbol, molecular weight, solubility in 100 parts of cold water, boiling water, cold alcohol. For instance, we find in the above order:—Sodium thiosulphate; 31, 46, 54, 77, 78, 121; hyposülphite of soda, "hypo"; $Na_2S_2O_3+5H_2O$; 248; 100; very soluble; insoluble.

The book is handy in form and printed in clear type, and will, we feel sure, meet with the success it deserves.

The Production of Precious Stones in the United States in 1896. By George F. Kunz. Washington: Government Printing Office. 1897. Pp. 39.

The most important events in connection with precious stones during the year 1896 are stated to be the presentation of some interesting conclusions as to the origin of certain diamonds found in Wisconsin by Prof. Hobbs; the publication of Prof. Carvill Lewis's conclusions as to the genesis of the diamond; the finding of sapphires in Montana, equal in colour to, though smaller than, the best Ceylon gems; the continued finding of tourmalines, beryls, and turquoises; and the visit of M. Moissan to the United States to deliver his lecture on artificial diamonds.

The above-mentioned subjects are all given at considerable length in these pages, together with a good deal of other interesting matter, with regard to the finding of precious stones in other parts of the world.

A list of the values of the different gems and precious stones found in the United States during the year 1896 is given at the end, and we note that the turquoise comes first, at 40,000 dollars, followed by sapphire and gold quartz at 10,000 dollars each, and so on down to dumortierite in quartz at only 50 dollars, the grand total for thirty-eight separate kinds being 97,850 dollars.

The Commercial Uses of Coal-Gas. By Thos. Fletcher, F.C.S. London, Warrington, and Manchester: Fletcher, Russell, and Co., Lim. Pp. 104.

The name of Fletcher in connection with gas-stoves is so well known—throughout certainly the English-speaking world—that many lines are not required to describe the handy little book now before us. It must not be thought that this is anything like the well-known laboratory catalogues,—far from it; it is devoted to the economical consumption of coal-gas in its widest sense, as applied not only to heating rooms and cooking, but to the arts and manufactures in every direction; to heating bookbinders' tools and printers' rollers; to the prevention of burglary and the hardening of steel; to bacon drying and smoke abatement; and other objects too many to specify. Mr. Fletcher has done much for the improvement of gas consumption, and deserves the thanks of many thousands of persons.

Handbook to the Workmen's Compensation Act, 1897. By M. Roberts-Jones, Barrister-at-Law. London: 82, Fleet Street. Cardiff: Western Mail, Lim. Third Edition. Pp. 860. 1897.

Large employers of labour will find this handbook of great value, by enabling them to ascertain more clearly how the Workmen's Compensation Act works in practice. It is beyond our province to discuss in these columns the wisdom or fairness of the Act; it is enough that it is law, and must be conformed to. Ignorance being no excuse in the eye of the law, a work of this character is of great assistance to those who, through no fault of their own, may become liable to pay damages in respect of accidents. A number of cases are cited which have already come before the courts, and schemes are given whereby the masters and men can arrange a basis of compensation by mutual consent; such schemes, of course, being subject to the approval of the Registrar of Friendly Societies.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxv., No. 26, December 27, 1897.

Constitution of Phthalic Green.—A. Haller and A. Guyot.—The authors have attempted to attribute a formula to phthalic green which would be in harmony with that of diphenylanthrone. Taking analogy into consideration, they think that the green should come from the chlorhydrate of hexamethyltriamidodiphenylanthrone, but this does not altogether fit in. Eventually they decide to adopt the formula suggested to them by M. Rosenstiehl, $Cl\gtrless C\lesssim^{C_6H_4N(CH_3)_2}_{C_6H_4N(CH_3)_2}$, which makes of their molecule $C_6H_4\lesssim^{C\,O\,C_6H_4N(CH_3)_2}$ a malachite green substituted in ortho by $COC_6H_4N(CH_3)_2$.

Preparation of Alloys of Glucinum. Alloys of Glucinum and Copper.—P. Lebeau.—Alloys of glucinum have been prepared by reducing the oxide of glucinum in the presence of another oxide or a metal. When a mixture of oxide of copper, oxide of glucinum, and carbon is heated in the electric furnace, a well-melted ingot is obtained being an alloy of these two metals. The proportions used in two experiments were—

	I.	II.
Glucina	25 grms.	25 grms.
Oxide of copper ..	50 „	190 „
Carbon	10 „	25 „

In the first case, the resulting ingot weighed 45 grms.; and in the second case, 142 grms. Alloys containing about 10 per cent of glucinum are of a pale yellow colour, almost white; those containing 5 per cent are more yellow; they are easily worked and take a good polish.

Impurities in Aluminium and its Alloys.—Ed. de Facqz.—The insoluble residue left after attacking aluminium with hydrochloric acid was found to consist of oxides of iron and aluminium, silicon, and traces of copper.

On a Double Carbonate of Soda and Protoxide of Chromium.—G. Baugé.—When we add a solution of carbonate of sodium in boiled water to well-washed and still moist chromous acetate, we notice that the acetate immediately goes into solution, and that a reddish brown body is precipitated. This precipitation must be conducted in a current of carbonic acid quite free from oxygen. Chromous sodic carbonate forms two hydrates—one taking ten molecules of water, and the other only one. The former, when examined under the microscope, appears in the form of little reddish brown lozenges—either isolated, or grouped together like the leaves of a book. It is very efflorescent, and is an energetic reducing agent; it decomposes water below 100°, with the disengagement of hydrogen; it is soluble in cold water, but its solubility, however, decreases on keeping. The salt containing one molecule of water is a yellow powder, which changes to brown when heated *in vacuo* or in a current of hydrogen; it regains its yellow colour on cooling. It decomposes at about 300° into green sesquioxide and carbonate of sodium. Heated in the air, it quickly oxidises, forming chromates of sodium. Cold boiled water gradually transforms this salt into the one containing ten molecules of water. The formulæ for these two salts are—$CO_3CrCO_3Na_2,10H_2O$ and $CO_3CrCO_3Na_2,H_2O$.

Atomic Weight of Cerium.—MM. Wyrouboff and Verneuil.—A continuation of the discussion with M. Boudouard, in which the authors express the opinion that the differences between them and the last-named gentleman rests on a misunderstanding.

The Aromatic Diurethanes and Piperazine.—P. Cazeneuve and M. Moreau. — Piperazine gives urethanes of the form $CO<\begin{matrix}N<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}>N\\OR\qquad RO\end{matrix}>CO$; R being an aromatic radical. These are veritable diurethanes formed in virtue of the repetition of the amine group in the molecule.

Use of Carbide of Calcium for the Preparation of Absolute Alcohol.—P. Yvon.—Will be inserted in full.

On α-Acetylfurfurane and its presence in Stockholm Tar.—L. Bouveault.—α-Acetylfurfurane, whether produced synthetically or extracted from tar, is identical both in crystalline form and chemical properties; they each form a crystalline oxime melting at 104°.

Behaviour of a Mixture of Pyridine with Propionic, Acetic, and Formic Acids during Distillation.—G. Andié.—There is evident combination between these acids and pyridine, for at the moment of mixing there is a considerable disengagement of heat.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xvii.-xviii., Nos. 20-21.

Dissociation Spectra of Melted Salts. Metalloids: Chlorine, Bromine, Iodine.—A. de Gramont.—Already inserted in full.

Reduction of Molybdic Anhydride by Hydrogen, and the Preparation of Molybdenum.—M. Guichard.—In view of the contradictory results obtained by different chemists, and to decide which oxides among Mo_2O_5, Mo_5O_{12}, MoO_2, Mo_2O_3 can be obtained by the action of hydrogen of MoO_3, the author took up the research methodically. M. Moissan has shown that the three most important factors in such an operation are the rate of flow of the gas, the temperature, and the time. As a rule, the higher oxides pass through intermediate stages before being reduced, but each oxide has a temperature below which reduction does not take place. Hydrogen, washed with chromic acid and dried with potash, was passed over red-hot copper, dried again, and passed through a U tube containing the oxide to be reduced, the U-tube being kept in a bath of melted tin. On slowly heating molybdic anhydride in hydrogen, the colour changes as the temperature rises to yellow, grey, bluish grey, and violet-brown, until eventually, when a red heat is reached, it is entirely of a metallic grey colour. The temperatures at the different colours have been found experimentally not to exceed 600°, and the author has also proved that there are only two anhydrous oxides, MoO_3 and MoO_2, the others previously mentioned not being definite compounds.

Modification of Friedel's and Crafts's Method giving a Higher Return in Syntheses made by the Help of Chloride of Aluminium.—A. Verley.—A long paper not suitable for abstraction.

Action of Nitrate, Sulphate, Chlorate, and Phosphate of Ammonia on Aspillergus Niger.—C. Tanret.—The author is of the opinion that aspillergus and the higher plants ought equally to be able to get rid of the mineral acids which are of no use to them, and that the acid excretion which has been observed in their radicells should be due to these acids, either in the free state or in combination with organic matters.

No. 22.

Some New Experiments on the Liquefaction of Fluorine.—MM. Moissan and J. Dewar.—Already inserted in full.

Chromosulphochromic Acids. Alkaline Chromosulphochromates.—A. Recoura.—The author describes certain compounds analogous to those formed by the combination of the green sulphate of chromium with sulphuric acid, but in this case with chromic acid and the chromates. The existence of these compounds can easily be shown by adding a solution containing one molecule of $Cr_2,3SO_4$ to a solution containing one molecule of chromic acid or chromate of potash; the combination takes place immediately, and that the sulphuric and chromic acids are both assimilated is proved by the fact that neither chloride of barium nor nitrate of silver will give a precipitate. The same combination of the green sulphate can be shown with two molecules of chromic acid or chromate of potassium; and the chromosulpho-dichromate of potassium, when dried at 150°, is, like the monochromate, insoluble in water. In a similar manner chromosulpho-trichromic acid can be obtained, but the combination stops here, for if four molecules be added a precipitate is obtained by nitrate of silver, when all the other conditions are exactly the same as before.

Action of Oxygen on Dissolved Formic Aldehyd.—Marcel Delépine.—Although oxygen has no action on an aqueous solution of formic aldehyd at ordinary temperatures, if it is warmed up to 200° the whole of the oxygen enclosed in the tube is absorbed. The presence of potash in the cold, or even at 100°, will not cause the oxidation of dissolved formic aldehyd, but in the presence of spongy platinum complete oxidation—a veritable combustion—takes place at the ordinary temperature.

Action of Chloride of Ethylalcohol on the Aromatic Hydrocarbides.—L. Bouveault.—A number of new organic compounds are described, but the paper is hardly suitable for abstraction.

Glyoxylic Acids and Aldehyds derived from the Phenol Ethers.—L. Bouveault. — Not suitable for abstraction.

On Phenol-Glyoxylic Acids.— L. Bouveault. — The simple phenols give no reaction with chloride of ethyl-oxalyl and chloride of aluminium, neither do the radical-acid ethers of the phenols; but the best results have been obtained with the ethers formed by picric acid. Several of these compounds are described.

On some Derivatives of Guïacol.—L. Bouveault.—The unsuccessful attempts made by the author to effect the synthesis of vanilline caused him to prepare several ether derivatives of guïacol, which are here described.

Volumetric Estimation of Combined Sulphuric Acid. — Felix Marboutin and Marcel Molinié. — The authors have undertaken to determine the corrections necessary, in the Windisch method, of estimating sulphuric acid volumetrically, on account of the unavoidable non-equivalence of the two solutions used, viz., chloride of barium and chromate of potassium. In their experiments they used N/50 solutions, but the chromate was of a little higher value than the barium; the figures they obtained were compared with those of the gravimetric method, and a large table given enables us to compare the relative values of the two volumetric methods, and it appears that the new modified method is superior in exactitude to that of Windisch.

Volumetric Estimation of Combined Sulphuric Acid.—Felix Marboutin.—To estimate the sulphates in potable waters, 100 c.c. of the water is acidulated with hydrochloric acid, and boiled to drive off the carbonic acid; the temperature is then slightly lowered, and 30 c.c. of chloride of barium is added, drop by drop; then let stand at 40° to settle; it is then neutralised with a few drops of ammonia, and 30 c.c. of chromate of potassium added; the liquid is made up to 300 c.c. after cooling. To 100 c.c. of the clear liquid is added 2 c.c. of 25 per cent sulphuric acid and 5 c.c. of arsenious acid, it is then warmed and shaken till the colour disappears. After neutralising with carbonate of potassium, titrated iodine is added until starch is coloured. This method has the advantage of requiring no filtration or washings, and it takes into account any impurities in the reagents, and they need not, except the iodide, be very carefully titrated beforehand.

MISCELLANEOUS.

Nottingham University College.—The Retirement of Dr. Clowes.—An interesting little ceremony took place last evening at the Nottingham University College, when a number of the past and present chemical students, together with the chemical staff of the college, assembled for the purpose of making a presentation to Dr. F. Clowes. Until recently Dr. Clowes occupied the chair of chemistry at the University College, which he has held since the opening of the institution 16 years ago. He recently resigned the position in order to assume the office of chemical adviser and chief chemist to the London County Council. The Rev. Principal Symes presided, and among those also present were Prof. Granger, Prof. Robinson, Dr. Clowes, Dr. Kipping, and Dr. Sudborough. The presentation consisted of a handsome silver kettle for the tea-table, and ornamental silver candlesticks. The Rev. Principal Symes alluded to the ability and patience which Dr. Clowes had displayed during the sixteen years he had been engaged at the college. In earlier years the institution had to pass through a period of exceptional difficulties, and they owed to Dr. Clowes a deep debt of gratitude for his tact and courtesy during those days. (Applause). Those were very critical times, when the very existence of the college was at stake. The governing body of the institution had just testified to their sense of appreciation of the work which had been accomplished by Dr. Clowes, by bestowing upon him the title of *emeritus professor*. (Applause). In conclusion, Professor Symes said that they all wished for Dr. Clowes a long and useful career in his new sphere. They were sure that if it was lengthy it would be useful. (Applause). Dr. Sudborough and representatives of the past and present chemical students also spoke. Dr. Clowes acknowledged with deep gratitude the handsome presentation, which, valuable in itself, would serve to him as an invaluable memento of kindly feelings entertained towards him by those with whom he had been associated as fellow worker for sixteen years. His own chemical department had been more especially dear to him, and his relationship towards staff and students in that department had always been one of personal and individual friendship. This kindly and generous reception of his work had rendered his duties a real source of enjoyment to him, and would always be remembered by him with pleasure. It resulted in his meeting friends, who had been associated with him as fellow teachers or pupils in all parts of the country, and, indeed, of the world. (Applause). After nearly twenty-five years spent in active tuition, he was not sorry to assume advisory and consultative duties only. In his new sphere, acting as chemical adviser and chief chemist to the London County Council, he had the direction of a staff of over forty assistants, most of whom were qualified chemists, and he hoped that he might, therefore, be able to find useful employment for some of those who had received their chemical training in the Nottingham College. The position involved advice and investigation in connection with chemical problems of the most varied description, but it included the constant examination of the metropolitan gas and water supplies, the provision of the best means for disposal of the London sewage, and the maintenance of the purity of the Thames, more especially in its tidal portion. For the performance of these duties twenty gas-testing stations were provided, in which daily tests were carried out and reported to the chief chemist; two chemical laboratories at the sewage outfalls, whence the results of the chemical examination of the sewage effluent into the Thames and of the tidal Thames were periodically reported, and a central laboratory at Charing Cross, in which general chemical analysis and investigation were constantly being carried out. As a result of the past work in this chemical department, the condition of the gas supply to London had been vastly improved, and the Thames had ceased to be a foul offensive stream within the metropolitan reaches, whilst the use of bad mortar by the jerry-builder and the introduction of dangerous petroleum has almost ceased. It is hoped that ere long the fish, which had now made their appearance again in the tidal portions of the river, would be able to pass through London to the upper stream. In conclusion, Dr. Clowes mentioned the general scope of his new duties, for the reason that many of his friends in Nottingham were asking for the information. They were duties which, connected as they were with a population of nearly five millions, would prove engrossing and important, but he was sure, that while engaged in the large sphere, memory would frequently transport him to the period of happy work carried out in Nottingham. (Applause).

Institute of Chemistry January (1898) Examinations.—*Names of Candidates who passed the Practical Examination for the Associateship* (under Regulations in force prior to October 1st, 1893).—William Alfred Caldwell, Glasgow and West of Scotland Technical College; Alfred Campion, jun., Finsbury Technical College, London; George P. Darnell-Smith, B.Sc. (Lond.), University College, London, and under Professor J. Wertheimer, F.I.C., Merchant Venturers' Technical College, Bristol; Albert Edward Thomas, registered student under Professor J. Wertheimer at the Merchant Venturers' Technical College, Bristol; Alfred John Turner, Finsbury Technical College, London.

Final Examination for the Associateship (New Regulations).—In Section "A" (General Inorganic Chemistry):

Alexander Hugh Dewar, Glasgow and West of Scotland Technical College. In Section "B" (the Chemistry of Metals and Alloys): Albert Lucas Entwistle, Owens College, Manchester, and registered student under T. J. Hutchinson, Esq., F.I.C. In Section "D" (Organic Chemistry): Bertram William John Warren, Mason College, Birmingham, and Finsbury Technical College, London. In Section "E" (the Chemistry of Water, Food, and Drugs): Edwin James Read, B.A. (Cantab), Cambridge University.

Intermediate Examination (New Regulations).—Norman Parr Booth, Mason College, Birmingham; Charles Adolphus Hackman, King's College, London, and with A. C. Chapman, Esq., F.I.C.; Leonard Myddelton Nash, King's College, London, and with Bertram Blount, Esq., F.I.C.; Roland Cecil Wild, King's College, London, and registered student under C. J. Head, Esq., F.I.C.

The Royal Photographic Society is organising an International Exhibition of Photographic Apparatus and Photographs, which will open at the Crystal Palace on April 27th. In addition to the usual displays of pictures, &c., the leading firms, manufacturers, and dealers will be largely represented. There will also be extensive loan collections, illustrating not only the history of photography, but its enormous scientific and commercial applications, photo-mechanical processes, photographs in colours, photographs by means of the X-rays, and kindred exhibits. The Exhibition, the arrangements for which are in the hands of a joint committee of members of the Society and exhibitors, bids fair to be the largest and most interesting collection dealing with photography which has ever been got together.

The Sanitary Institute.—The Council have accepted an invitation from the Lord Mayor and City Council of Birmingham to hold its Seventeenth Congress and Exhibition in that city in September next.

Nature of the Compounds of Antipyrin with the Aldehyds. — G. Patein. — Antipyrin combines with aldehyds; the union being effected by carbon, never by nitrogen. In these compounds, which are true derivatives of methane, the atom of nitrogen united to methyl loses the power of combining with chloral and the phenols. Chloral, or trichloric aldehyd can unite with antipyrin only by means of nitrogen, and never by carbon, like the non-substituted aldehyds.—*Comptes Rendus*, vol. cxxv., No. 23.

MEETINGS FOR THE WEEK.

MONDAY, 31st.—Society of Arts, 8. (Cantor Lectures). "Decorative Bookbinding," by Cyril Davenport.

TUESDAY, Feb. 1st.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.

WEDNESDAY, 2nd.—Society of Arts, 8. "The Cinematograph," by Jules Fuerst.

—— Society of Public Analysts, 8. Annual Meeting (to be held at the Chemical Society's Rooms, Burlington House). President's Address. "Copper, 'Pure for Analysis,'" by J. W. Westmoreland. "Note on the Tests for distinguishing Boiled from Unboiled Milk," by H. Leffmann, M.D. Election of Officers and Council.

THURSDAY, 3rd.—Chemical, 8. "On the Dissociation of Platinichloride in Dilute Solution, and the Production of Platinum Monochloride," by E. Sonstadt. "Effect of the Mono-, Di-, and Tri-chloracetyl Groups on the Rotatory Power of Methylic and Ethylic Glycerates and Tartrates," by Percy Frankland, F.R.S., and Thomas Stewart Patterson, Ph.D. "The Rotation of Ethylic and Methylic Di-monochloracetyltartrates," by Percy Frankland, F.R.S., and Andrew Turnbull, Ph.D. "The Volumetric Estimation of Sodium," by H. J. H Fenton, M.A.

— Royal Institution, 3. "The Halogen Group of Elements," by Prof. Dewar, M.A., LL.D.

FRIDAY, 4th.—Royal Institution, 9. "Some New Studies in Cathode and Röntgen Radiations," by A. A. C. Swinton.

SATURDAY, 5th.—Royal Institution, 3. "Cyprus," by Prof. Patrick Geddes, F.R.S.E.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Destruction of Moths.—(Reply to "Moth-eaten").—One of my friends, a physician, tells me that he placed an Astrachan fur cloak already attacked by moths in a tin receptacle, introduced 10 c.c. of formalin (asserted to contain 40 per cent of formic aldehyd), and covered and sealed the tin with care. After a considerable time he opened the tin, when out flew a cloud of moths. My friend is a bacteriologist; he finds that formaldehyd is destructive to many forms of bacteria, but by no means to all; and, so far as his experience has gone, it has but little effect upon animal life such as moths and other household pests.—ELWYN WALLER, New York, U.S.A.

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THE RESEARCH SOCIETY.

IN Appendix F to Part II. of the new edition (1890) of Thomson and Tait's "Treatise on Natural Philosophy" the Kinetic Theory of Gases is stated to be "an established truth of science."

At page 226 of Vol. I. of Lord Kelvin's "Popular Lectures and Addresses" (*Nature* Series) there occur the words—"What we now accept as a surest article of scientific faith —the Kinetic theory of gases."

In §22 of the "Text-book of Physical Chemistry'" (1897), by Prof. Clarence L. Speyers, of Rutger's College, the statement is made that "The Kinetic theory is a troublesome thing and is becoming an object of ridicule. It has never directed the chemist to any new discovery or idea, unless it may be Van der Waal's theory, and that would probably have come anyway."

These quotations amply suffice to establish the need that exists for a school of philosophy based upon the *facts* of Nature as distinguished from the mere utterances of Authority.

(In saying this no disrespect is intended to Lord Kelvin and Prof. Tait. They deservedly rank high in the hierarchy of Science. But if Prof. Speyers be correct in his description of the Kinetic theory of gases, it follows that much of the teaching of Thomson and Tait is misleading).

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 1993.

SEPARATIONS FROM CHROMIC ACID.

I. The Separation of Iron.

By HARRY BREARLEY.

a. *A Reaction between Ferric Salts and Alkaline Chromates.*

In a former paper (Chemical News, lxxvi., p. 175) it was pointed out that a customary means of separating iron and chromium, viz., precipitation of the former as basic acetate after oxidising the latter to chromic acid, contained an inherent source of error. This was traced to a reaction between solutions of ferric chloride and alkaline chromates, which it is now proposed to examine more closely.

In another form, or degree, this reaction is already well known, having been observed as early as 1829, and subsequently studied by a number of chemists. In 1862 Storer and Eliot (Chem. News, vi., p. 12) again observe the reaction and summarise the work of previous observers.

It should, however, be mentioned that the reaction between ferric chloride and potassium chromate occupies quite a secondary place in the preceding researches. The chief aim was to determine the composition of the precipitate formed by adding potassium chromate to a solution of a salt of chromic oxide. Storer and Eliot's title, "On the Chromate of Chromium and Analogous Chromates," is sufficiently expressive of the central interest.

The reaction between solutions of the salts of CrO_3 and Cr_2O_3 was known to Vauquelin, the discoverer of chromium, and twenty years later, guided by the analogy of chromium and iron, Thompson prepared a compoumd of chromic acid and ferric oxide. This he found to be very basic $(Fe_2O_3)_5{\cdot}CrO_3$, and in the filtrate and wash-waters he thought he found another less basic chromate, $(Fe_2O_3)_2{\cdot}CrO_3$.

A great deal of work was done with an eye to determining whether the chromic acid and chromic oxide compound should be viewed as an oxide, CrO_2, or as a chromate, $Cr_2O_3{\cdot}CrO_3$. The latter view was supported by analogy with $Fe_2O_3{\cdot}CrO_3$, $Al_2O_3{\cdot}CrO_3$, and $Mn_2O_3{\cdot}CrO_3$, all of which are said to be less stable compounds than $Cr_2O_3{\cdot}CrO_3$; and this even cannot be washed with water without being changed into a more and more basic compound approaching finally to Cr_2O_3.

It is manifest that these precipitates could be prepared of the required basicity only by mixing *concentrated* solutions of the two salts. In this respect the conditions differ from the usual iron-chromium separation. The only other points of difference are that in the latter case the iron is largely present as dissolved hydrate, and a reagent (alkaline acetate), whose presence it might be supposed would easily overcome the feeble affinity between the iron and chromium, is added for the express purpose of precipitating the iron. Some such fallacious reasoning would seem, in the first place, to have shielded a chromium-iron separation from suspicion; for later times we see occasionally in chemistry, as elsewhere, that "was grau vor Alter ist, das ist ihm gottlich."

It is too much to say that an error has never been suspected. The considerable abandonment of the method shows that it has, but that the method was fundamentally unsound does not seem to have entered into anybody's reckonings, and later references will show that it is still so far trusted as to beget yearly one or two modifications.

In pointing out the shortcomings of this method it seemed proper to test the matter under such conditions as obtain in practice, and to neglect its relation to the wider questions mentioned above. These conditions are dilute solution, and iron as ferric chloride and as dissolved ferric hydrate.

This arrangement permits the iron to become allied with the chromate in two ways:—1st, with ferric chloride in a manner strictly analogous with the procedure of Storer and others; and 2nd, the ferric chloride having been decomposed, by reacting with the ferric hydrate. The consequent changes are considered separately.

a. *Reaction with Ferric Chloride.*

The reaction for the production of $Fe_2O_3CrO_3$ has been formulated so:—

$$Fe_2Cl_6+5K_2CrO_4=6KCl+2K_2Cr_2O_7+Fe_2O_3{\cdot}CrO_3,$$

and, according to Storer, until the requisite amount of chromate has been added the precipitate once formed re-dissolves,—if the solution is cold. In a hot solution, however, a precipitate forms when only about one-fourteenth part of this chromate is present.

Thus, using 1 grm. of iron as ferric chloride and 50 c.c. of a K_2CrO_4 solution (12¼ grms. per litre), in a volume of 1 litre it was found that on boiling a precipitate formed, which, although unfilterable, settled completely after standing several days, and an analysis of the decanted solution showed that the precipitate contained chromium equivalent to 29·2 c.c. of the K_2CrO_4 solution, and iron equal to only 0·6527 grm. With intent to effect a more complete separation of the iron there was added 70, 100, and 120 c.c. of the chromate. The solutions were allowed to cool and settle, although with 70 c.c. and upwards filtration is possible. Table I. shows the relative composition of the precipitates, determined by analysing an aliquot part of the clear supernatant solution.

Table I.

	In precipitate.	
Chromate added.	C.c. chromate.	Grm. iron.
50 c.c.	29·2	0·6527
70 ,,	40·3	0·7848
100 ,,	44·0	0·7609
120 ,,	46·3	0·7137

As the two latter ones had been standing two or three days, it seemed likely that the cold solution had re-dissolved the precipitate. This was found to be the case, and, moreover, it was found that the precipitate re-dissolves more and more as it stands, and is shaken from day to day; and not the CrO_3 only, as some writers would lead one to infer, but the iron also is dissolved. At first the precipitate seems to become less and less basic, and then the iron and chromium are dissolved proportionately and the composition of the precipitate remains constant; but this composition varies with the amount of K_2CrO_4 originally used as precipitant. These changes, interesting enough in another connection, have, however, very little to do with the present purpose.

b. *Reaction with Ferric Hydrate.*

An acid solution of ferric chloride, representing 1 grm. of iron, was precipitated from a hot solution, with an equivalent amount of soda carbonate, the chromate added, solution made up to a litre and boiled. The results are shown in—

Table II.

Chromate added.	Recovered from filtrate.	In precipitate.
10 c.c.	2·0 c.c.	8·0 c.c.
30 ,,	16·2 ,,	13·8 ,,
50 ,,	34·2 ,,	15·8 ,,
100 ,,	81·6 ,,	18·4 ,,

It is proper to draw attention to the fact that in each of the above cases the supernatant chromic liquid was sepa-

rated by fractional filtration. It is common, however, although more tedious, to filter completely and wash the precipitate. Such a procedure might have shown a more complete separation in some of the cases, but it could hardly have made up the deficiency, because, presuming that all the cohesive liquid was removed, the basic chromates are decomposed only very slowly by washing. In the present case, too, when the washings ceased to be alkaline, the precipitate might also be dissolved (Table I.) as well as decomposed.

β. The Relation of the Reaction to some Analytical Methods.

Our attention was drawn to this matter by attempting to separate iron and chromium by means of soda acetate. This method is usually attributed to Gibbs. It is stated fully in the CHEM. NEWS (xi., 101). It is to be found also in Crookes's "Select Methods," Fresenius's "Quantitative Analysis," "Industries" (1893), and in other publications, so that it has probably been extensively used.

From a former paper (CHEM. NEWS, lxxvi., 175) it appears that the larger the amount of acetate used the greater the percentage separation; but it required impracticable amounts to effect even an approximate separation of the chromate from large amounts of iron. In each of these cases the solution contained 1 per cent or more of acetic acid, which did not appear to be advantageous. Its entire absence, in fact, might be desirable if such a circumstance could accompany the separation of iron as basic acetate at boiling temperatures. At lower temperatures, however, ferric acetate may be precipitated without decomposition, and it might be worth while to observe the separation of iron and chromium in this manner, if more promising and less troublesome means were not at our disposal.

As I have said, the shortcoming of this method has been recognised, and there have been proposed a number of methods in which either the oxidant or the precipitant or both are replaced by others. Thus, looking over former numbers of this journal and some recent issues of other journals, I tabulate the following:—

Oxidised with—	Separated iron with—
I.—Gibbs (CHEM. NEWS, xi., 101)—	
Chlorine, bromine, or lead peroxide.	Soda acetate or ammonia hydrate.
II.—Sell (CHEM. NEWS, liv., 299)—	
Hydrogen peroxide.	Potash.
III.—Baubigny (CHEM. NEWS, l., 18)—	
Nitric acid and potassium chlorate.	A very slight excess of soda bicarbonate.
IV.—J. Clarke (*Journ. Chem. Soc.*, 1893, p. 1082)—	
Soda peroxide.	Peroxide added to alkalinity.
V.—Marchal and Wiernik (*Journ. Chem. Soc. Abs.*, 1893, ii., 49)—	
Freshly precipitated and well-washed MnO_2 in neutral liquid.	Boiling.
VI.—Giorgis (*Journ. Chem. Soc.*, Abs., 1893, xi., 554)—	
Permanganate in slightly alkaline solution.	
VII.—E. Clarke (*Journ. Amer. Chem. Soc.*, 1895, p. 327)—	
Nitric acid and potassium chlorate.	Ammonia.

The following notes are abstracted from the respective papers:—

II. The context leads one to infer that only a small excess of potash was used. The results are shown to be low, and are attributed to part of the chromic hydrate escaping oxidation.

IV. "When applied to liquids containing a good deal of iron the results are generally somewhat low, even when the iron is precipitated twice in this way." Poleck (CHEM. NEWS, lxix., 285), and Kassner (*Journ. Chem. Soc.*, Abs., 1894, ii., 429) base a like process on the same facts.

V. The authors state that the processes of Wohler (oxidation with Br or Cl and precipitation of Fe with soda hydrate) and Gibbs both fail, even qualitatively, if the amount of chromium is small. The abstractor states that the test analyses, made on rather small quantities, are fairly satisfactory.

VII. "To render the separation complete the precipitate must be re-dissolved and re-precipitated by ammonia."

The following series of experiments help to explain the various opinions, to point out a source of error, and to suggest means of obtaining uniformly accurate separations.

It would be in order to severally examine the efficiency of the oxidants to completely oxidise the Cr_2O_3 to CrO_3 in presence of much iron. Certainly they are not all equally effective; some may even be defective. But apart from this there is a source of error—almost certain error—which previous experience leads us to expect, viz., the formation of basic ferric chromates. These, it might be presumed, would be greater or less according to the nature and amount of alkali used to precipitate the iron. Experiments dealing with this part of the subject are summarised in Table III. Each test contained 1 grm. Fe, 30 c.c. K_2CrO_4 (12½ grms. per litre), and a volume of 1 litre. The alkali used was in each case 2-normal strength.

TABLE III.

Excess of alkali.	Percentage separation. Sod. carb.	Sod. hyd.	Ammon. hyd.
0	54·6	69·3	24·8
10	90·4	100·0	70·4
20	97·5	99·8	77·0
30	98·7	100·0	83·6
50	100·1	—	87·8

The figures seem to indicate that either of the precipitants would give a perfect separation if enough of it was used. Soda hydrate is, however, by far the most practicable, and this it will be remembered is the precipitant recommended in Wohler's method.

The analogy in so many respects between iron, aluminium, chromium, and manganese, leads one to think that an examination of these metals in turn, with respect to their separation from chromic acid by the usual methods, may not be unfruitful.

These observations, along with others on the use of alkaline chromates as precipitants, will form the matter of subsequent papers.

ON THE COLOUR OF AMORPHOUS MERCUROUS IODIDE.

By MAURICE FRANCOIS.

INCIDENTALLY I showed in a preceding article (*Journ. de Pharm. et de Chim.*, [6], Nov. 15, 1897), that a solution of mercurous nitrate transforms mercuric iodide into mercurous iodide of a pure yellow colour; we know, on the other hand, that dilute nitric acid easily dissolves finely divided mercury. In view of these two facts it did not appear to be difficult to devise a method for the preparation of pure mercurous iodide free from both free mercury and mercuric iodide. All that is required is that the mercurous iodide shall be formed in the presence of free nitric acid, and mercurous nitrate in considerable excess. This iodide should be of a very pure yellow colour. To effect this we weigh out 125 grms. of air-dried mercurous nitrate, and dissolve it in two litres of water containing 20 c.c. of

nitric acid. To the clear liquid add, drop by drop, from a burette while constantly stirring, a solution of 50 grms. of iodide of potassium in 100 c.c. of distilled water. The quantity of iodide of potassium necessary to precipitate all the mercury would be theoretically 75 grms.

Each drop as it falls produces a grey stain (local excess of KI), becoming yellow on stirring.

After having run in all the iodide of potassium, the liquid must be vigorously shaken for about fifteen minutes, so as to maintain the closest contact between the precipitate and the mother liquors. The precipitate, at first of a greenish yellow colour, has become much brighter. The whole is then left for twenty-four hours in complete darkness, and shaken up at intervals three or four times. After the lapse of this time, the precipitate is of a very pure bright yellow colour (similar to that of the yellow chromate of lead); it is then washed ten times by decantation, still in the dark, using two litres of water for each washing. The precipitate is finally collected on a filter, drained and dried at 50°, still in the dark.

Any washing with alcohol or ether is quite useless, and would change the character of the substance instead of purifying it. The iodide thus obtained is free from nitrate, mercuric iodide, and free mercury. On analysis it has been found to consist of:—

Found (per cent).		Theory (per cent).	
Mercury ..	61·06	Mercury ..	61·16
Iodine ..	38·96	Iodine ..	38·84

Having, on several occasions, had in my possession pure amorphous mercurous iodide, of a pure bright yellow colour, without any tinge of green, I was led to enquire what is the colour of pure mercurous iodide.

The generally accepted opinion is that the colour of amorphous mercurous iodide is a greenish yellow. Boullay even called this iodide *the green iodide of mercury*. M. Raoul Varet (*Comptes Rendus*, vol. cxx., pp. 1054-1114) made a distinction between the yellow mercurous iodide and the green mercurous iodide, and he moreover determined the amount of heat which corresponds to the passage of one of these modifications to the other. The commercial samples of amorphous mercurous iodide certainly show a considerable variation in tint.

For the purpose of getting at the root of the question, I analysed a certain number of samples prepared by different methods, and varying in colour from a pure yellow to a dark green. I now give the results of the analyses, together with the methods of preparation:—

I. Bright yellow mercurous iodide (chrome yellow colour), prepared by the action of iodised potassic iodide on mercurous nitrate (see my previous paper). Found:—Mercury, 61·29 per cent; iodine, 38·51 per cent.

II. Bright yellow mercurous iodide (chrome yellow colour), prepared by the action of iodide of potassium on mercurous nitrate, as I have just described above. Found:—Mercury, 60·96 per cent; iodine, 38·90 per cent.

III. Yellowish green mercurous iodide, prepared by the direct action of iodine on mercury, by following exactly the method described in the Codex. Found:—Mercury, 62·96 per cent; iodine, 36·74 per cent.

IV. Another greenish yellow mercurous iodide, prepared by the direct action of iodine on mercury. Found:—Mercury, 63·90 per cent; iodine, 36·00 per cent.

V. Dark green mercurous iodide, prepared by the action of iodide of potassium on calomel.

Found.—Mercury, 82·46 per cent; iodine, 12·11 per cent; chlorine, 5·35 per cent.

Theoretical for Hg_2I_2.—Mercury, 61·16 per cent; iodine, 38·84 per cent.

As can be seen from this table, which I have purposely cut as short as possible, if the two first specimens can be regarded as pure, then the three last vary considerably from the theoretical composition.

Further, the difference between the weight of mercury found and the theoretical weight does not indicate the quantity of free mercury present in the sample. To arrive at this excess, it is necessary to calculate the quantity of this metal required by the iodine found to form mercurous iodide. The difference between the quantity found and the quantity calculated is the free mercury contained in the substance. For the last sample, the weight of mercury, combined with chlorine to form calomel, has also been calculated.

Thus we find that Sample III. contains 5·11 per cent, Sample IV., 7·22 per cent, and Sample V., 33·28 per cent of free mercury.

The presence of an excess of mercury in Samples III., IV., and V. is, however, not astonishing.

In the preparation of mercurous iodide, by the direct action of iodine on mercury, we generally use (Codex) a slight excess of mercury, principally because the product is intended for medicinal purposes, and it is of importance that it should not contain any mercuric iodide. Several causes contribute to a still further increase in the proportion of mercury present. For instance, when the substance is prepared on a large scale, the mass heats and iodine is volatilised in great abundance. During the same operation, light causes the production of mercury and of mercuric iodide, which would be carried off by the subsequent washing with alcohol. Finally, this same washing still further enriches the product in mercury, as I have already shown (*Journ. de Pharm. et de Chim.*, vol. iii., p. 231, 1896). In the preparation by the action of iodide of potassium on calomel, the iodide of potassium is in excess with regard to the first portions of mercurous iodide formed, and we well know that it decomposes this body into mercury and mercuric iodide, which goes into solution.

Thus, mercurous iodide of a greenish yellow or green colour always contains a considerable quantity of free mercury. It seems to me only natural to conclude that it is the presence of free mercury which produces the green colouration, and that the colour of pure amorphous mercurous iodide is a bright yellow.

This opinion is supported by a number of old experiments, and some personal observations. For example:—

I. The green colour of various samples of mercurous iodide is different with each sample, tending sometimes towards the yellow, sometimes towards the grey, and verging sometimes on the black. That is not the behaviour of a pure body with a definite colour.

II. We can change the colour of mercurous iodide progressively from a bright yellow to a green by charging it with free mercury, as we actually do by adding small quantities of iodide of potassium to the yellow iodide suspended in water.

III. We can inversely change the green iodide to the yellow by removing free mercury from it; this can be done by two methods:—

(*a*). Into two flat-bottomed flasks we place 20 grms. of very green mercurous iodide (what was actually used was obtained by carefully acting on commercial mercurous iodide, with iodide of potassium, and then washing). Into one of these flasks we pour 50 c.c. of water (this flask is intended to serve as a check); into the other we pour 50 c.c. of dilute nitric acid (20 grms. of ordinary nitric acid and 80 grms. of water). These two flasks are kept in the dark, and well shaken every day. After several days we notice that the iodide, in the presence of the nitric acid, has become of a bright yellow colour.

(*b*). We place two grms. of green mercurous nitrate in a flat-bottomed flask, and as before prepare a check flask; add 100 c.c. of a normal solution of potassium iodide, saturated in the cold with mercuric iodide (this must be kept in the dark and well shaken every day). After a fortnight the mercurous iodide has assumed a very beautiful yellow colour. Evidently, in the first case, the free mercury has been changed into nitrate of mercury by the nitric acid; and in the second case, the mercuric iodide has transformed the free mercury into mercurous iodide. The free mercury disappearing, the iodide returns to its

natural colour, bright yellow. Analysis completely confirms these conclusions.

I cannot finish this article without thanking Professor Jungfleisch for the excellent advice which he has constantly given me, and which has aided me considerably in the course of this work.—*Journ. de Pharm. et de Chim.*, Series 6, vol. vi., No. 12, 1897.

ON THE USE OF CARBIDE OF CALCIUM FOR THE PREPARATION OF ABSOLUTE ALCOHOL.

By M. P. YVON.

When coarsely powdered carbide of calcium is brought into contact with concentrated alcohol (90 to 95 per cent) the carbide is fairly vigorously attacked, and continues to give off acetylene as long as any water remains in the alcohol; when the latter is quite anhydrous, the disengagement of gas ceases.

The use of carbide of calcium, therefore, enables us to determine whether or no an alcohol is anhydrous; it suffices, in fact, to place a few cubic centimetres of the alcohol in a perfectly dry test-tube, and then to drop in a pinch of the coarsely powdered carbide of calcium: if the alcohol is absolute, no gas bubbles whatever can be detected, and even after shaking the liquid remains transparent. If, on the contrary, the alcohol contains traces of water, we can see the little bubbles of gas forming, and on shaking, the mixture becomes cloudy and of a milky white appearance, on account of the formation of hydrate of lime.

To prepare absolute alcohol it suffices to place a quantity of alcohol at 90 or 95 per cent in a flask, with one-quarter its weight of carbide of calcium reduced to a coarse powder. The disengagement of gas, at first very vigorous, soon calms down; the flask is then frequently shaken up during two or three hours, and then left alone for twelve hours. It is then best to make quite certain that shaking no longer gives rise to any disengagement of gas; in the contrary case we prolong the agitation and the contact of the alcohol with the carbide, if necessary adding a little more of the latter; we then transfer the mixture to a distilling apparatus, and proceed with the separation of the alcohol, though putting on one side the first portions collected, as they hold a small quantity of acetylene in solution. It is advisable to keep the first portions far away from any flame, as they consist of a mixture of alcohol and acetylene. The alcohol afterwards collected is anhydrous, if the operation has been properly conducted.

It is preferable, however, to collect all the alcohol in the same receptacle, and then shake it up with a small quantity of dried sulphate of copper, which takes up all the acetylene held in solution. We can then proceed with a second distillation without separating the acetylide of copper which is formed.

Absolute alcohol prepared by this method is not precipitated by alcoholate of baryta; carbide of calcium is therefore as sensitive a reagent as this latter, and enables us to obtain absolute alcohol by one distillation, or two at the most, by starting with alcohol at 90 or 95 per cent.—*Comptes Rendus*, cxxv., No. 26.

Physical Society. — Mr. Thomas H. Blakesley has resigned his seat at the Council Board of the Physical Society. He is therefore no longer Honorary Secretary of that Society.

THE ANALYSIS OF BEARING-METAL ALLOYS. WITH A NEW VOLUMETRIC METHOD FOR DETERMINING COPPER.*

By W. E. GARRIGUES.

(Concluded from p. 41).

New Process for Copper.

This depends on the precipitation of the copper as cuprous thiocyanate according to Rivot, and the alkalimetric determination of the combined thiocyanic acid.

The solution is evaporated with as little sulphuric acid as possible to expel any volatile acids; warm gently after dilution, and add sulphurous acid until its presence is plainly apparent by odour. Precipitate with an alkali thiocyanate. When the liquid settles perfectly clear, which is promoted by further warming, filter and wash well with water.

Transfer the filter and contents back to the beaker in which the precipitation was effected, boil with a measured excess of standard caustic alkali, a few minutes is sufficient, then cool and dilute to a convenient bulk (200 c.c.). After passing through a dry filter, take of the filtrate a quantity equal to one-half the bulk of the original solution, and titrate to neutrality with standard acid and methyl orange.

The rationale of the process is that caustic alkali converts cuprous thiocyanate into cuprous hydroxide and alkali thiocyanate, the latter body being neutral to methyl orange. The reaction proceeds quantitatively according to the equation—

$$2CuSCN + 2NaOH = Cu_2(OH)_2 + 2NaSCN,$$

with all quantities of copper, one equivalent of caustic soda equalling one of copper. No requirement of an empirical standard is one of the advantages of the process. The writer claims for it greater accuracy than the iodide method is capable of.

Antimony is determined by Mohr's method: titration with iodine in alkaline solution, antimonic acid being previously reduced by the method of Gooch and Gruener (*Am. J. Sci.*, xlii., 233). This is very much to be preferred to the oxidimetric method again recently advocated by Thompson (*J. Soc. Chem. Ind.*, xv., 255), or to any attempt at separation from tin.

Lead is determined as sulphate, filtering on a Gooch with a paper disc, drying and weighing. In this manner the determination is capable of great accuracy, the drying being much better than ignition.

Tin is weighed as oxide, or in presence of antimony is determined by difference in weight.

Arsenic by Lundin's distillation process, as described by Blair in his work on iron analysis.

Phosphorus as magnesium pyrophosphate.

General Considerations.

When an alloy is treated with nitric acid, a more or less white residue remains insoluble. This contains all the tin, part of the antimony, iron, arsenic, phosphorus, copper, and lead, the two last, of course, only in small amount, though the copper may amount to several milligrms. No method of treatment has been found which gives this residue free from iron and copper. If all excess of nitric acid be evaporated, and the residue again taken up with dilute nitric acid, it is possible to retain all the iron in the residue, provided the tin is present in fair amount. The same applies also to the arsenic and antimony, though it is probably unsafe to count on this. In no event can the insoluble residue from a brass or bronze be considered sufficiently pure to weigh as stannic oxide. We separate the iron, copper, and lead from the tin and

* Read before the Chemical Section of the Engineers Society of Western Pennsylvania. From the *Journal of the American Chemical Society*, vol. xix., No. 12, December, 1897.

antimony by fusing with sodium thiosulphate and dissolving in water, preferring this to attempting to make the usual alkali sulphide separation in solution with all the copper and lead. The thiosulphate is a neater and quicker flux than sodium carbonate and sulphur.

If to save time in determining tin alone, when phosphorus, arsenic, and antimony are absent, it is desired to obtain the weight of stannic oxide by difference, the nitric acid insoluble residue may be ignited and weighed, fused with thiosulphate, dissolved in water, and the sulphides of lead, copper, and iron remaining removed by filtration. The filter is then moistened with nitric acid, and ignited in the same crucible (the fusion does not alter its weight perceptibly), subtracting the weight so found from the total weight of the residue. The difference is taken as stannic oxide.

A slight error must, however, be noted here: any lead present was weighed first as oxide, and afterwards subtracted partly or wholly as sulphate. It may be present to an extent that will make this error serious. If, on the other hand, the sulphides are not moistened with nitric acid, the iron is very likely to burn only to the magnetic oxide, where it was at first weighed as the peroxide, while the condition of the lead is indefinite.

In the case of a complete analysis of an alloy containing zinc, it is a great help to get all the iron out of the way at this early stage, and as the copper and lead must be returned to the main solution, it will be more troublesome to separate these, after igniting the sulphide precipitate, than to precipitate the tin directly as sulphide from the solution of the fusion, and converting to oxide for weighing. The latter also has the advantage that it is applicable in the presence of phosphorus.

Hempel (*Ber. d. Chem. Ges.*, xxii., 2478), referring to the separation of phosphorus from tin, states that some of the phosphorus invariably comes down with the hydrogen sulphide precipitate of the tin. Whether or not the same applies to the sulphide precipitate, obtained as a result of acidulating the dissolved fusion, we have not ascertained, but it seems probable that it would not. At any rate the amount is too small to practically affect a tin determination in phosphor bronze. Arsenic, however, will largely remain with the ignited tin precipitate unless previously separated.

When the nitric acid filtrate from the insoluble residue is evaporated with a little sulphuric acid to take out the lead, there results a further precipitation of antimony. The lead sulphate cannot be removed by solution in ammonium acetate, as the antimonic acid is likewise affected. A large excess of sulphuric acid prevents this second precipitation, but its presence is undesirable for the separation of copper as thiocyanate. A little tartaric acid added to the diluting water will also prevent it, and has, moreover, no effect on the copper precipitate, but this may cause the re-solution of a trace of lead. For ordinary purposes this amount is negligible, but at any rate it may be very easily recovered and added at a later stage.

Alloys containing antimony are usually poor in copper and free from zinc; exceptions, however, must be allowed for, and in the presence of both zinc and antimony the precipitation of copper as thiocyanate is not advisable, as the scheme thereby becomes complicated. Instead, the excess of sulphuric acid is used to prevent the precipitation, with the lead sulphate, of any antimony that remains in the nitric acid solution. In the filtrate from the lead sulphate the antimony and copper are thrown down together as sulphides, and separated with caustic soda. In the residue the copper may, of course, be determined by the thiocyanate process, but as it is free from any other metals it is directly available for titration by the iodide method. In the filtrate from the sulphides the zinc is obtained as phosphate. It should be remembered that if great accuracy is desired in the figure for zinc, the sulphide precipitate, after removing the antimony, is to be dissolved and again precipitated to insure against loss of zinc.

As a result of converting the mixed sulphides of tin and antimony into oxides for weighing, a slight error is sustained owing to the fact that the two sulphides require different treatment to give accurate results. By treatment with fuming nitric acid combined sulphur is oxidised completely, and the full heat of a good Bunsen burner will convert all pentoxide of antimony to tetroxide without any trouble, but while the tin precipitate requires a white heat to drive out the last traces of water, antimony will not stand this heat. If, therefore, the Bunsen flame be used, and one-tenth per cent be subtracted from each twenty per cent of tin found, the result is better than if the actual weight obtained is taken.

As the sulphides of tin and antimony are recovered from the dissolved fusion, they are mixed with considerable free sulphur, which cannot be completely oxidised with fuming nitric acid in one evaporation. For the most careful work washing the dried sulphides with carbon disulphide is necessary, but ordinarily, careful ignition will answer. After evaporating the mass to dryness with fuming nitric acid, and burning at a temperature just sufficient to ignite the sulphur, the residue is again moistened with fuming nitric acid for final ignition. This is important. The paper is, of course, to be consumed separately. A well-rounded inverted lid is used as a cover during the action of the acid.

When the ignited oxides of tin and antimony are dissolved by fusion with caustic (or carbonated) alkali, and obtained as higher chlorides in acid solution, potassium iodide reduces only the antimonic salt. We prefer to boil down twice to about fifty c.c. to insure the expulsion of the liberated iodine. We have found the colour of the liquid not a safe guide in practice, except that if perceptible deepening of the yellow takes place when approaching the bulk mentioned, the liquid must be immediately diluted, and the second evaporation not carried quite so far. Failure to do this will result in loss of antimony by volatilisation.

The separation with hydrogen sulphide of copper from zinc in hydrochloric acid is, according to Fresenius, rarely perfect. On testing a number of copper sulphide precipitates from solutions of brass containing fifteen c.c. strong hydrochloric acid in a bulk of 200 c.c. of liquid, we have never failed to find zinc in appreciable quantity. The precipitation as thiocyanate is, on the other hand, absolutely free from this source of error, and if the volatile acids are expelled with as small a quantity of sulphuric acid as possible, the amount of copper that escapes precipitation is infinitesimal. The precipitate cannot be dried and weighed with anywhere near the accuracy one might be led to suppose from the single experiment quoted by Fresenius. Such a procedure is quite out of the question.

The excess of ammonium thiocyanate exerts no deleterious action on the zinc precipitation with ammonium phosphate in the filtrate, and methyl orange is available as indicator for exactly neutralising the solution. When potassium thiocyanate is used the zinc precipitate is highly contaminated, so much so that it fuses at a low heat to a clear liquid, the results being entirely without value.

The Analysis of Bronze and Brass (Antimony being Absent).

Oxidise one grm. with strong nitric acid, and evaporate on the water-bath to complete expulsion of the acid. Take up with fifty c.c. three per cent nitric acid and filter after boiling five minutes. Ignite filter and contents together in a porcelain crucible, grind the residue with a thick glass rod, and fuse with a liberal addition of sodium thiosulphate. Leach out with a little water, digest until the liquid is clear yellow, and remove the precipitated sulphides by filtration. In the absence of arsenic, determine tin in the filtrate by acidulating with hydrochloric acid, filtering out the sulphide of tin, and washing with ammonium acetate. Ignite at low temperature, together

with the filter, raising the heat gradually after all free sulphur has been consumed, and finishing with a blast to constant weight.

The mixed sulphides of lead, copper, and iron, recovered from the fusion, are dissolved by boiling with twenty per cent nitric acid, from which solution the iron is thrown down by ammonium acetate. The filtrate is added to the main solution, and the whole evaporated with as little sulphuric acid as possible, the lead sulphate collected on a Gooch crucible and weighed.

In the filtrate the copper is thrown down as thiocyanate, and its value determined by the method described. The zinc is then obtained from the neutralised filtrate with ammonium phosphate, observing the precautions mentioned.

Phosphorus is determined in a separate portion by heating some time with aqua regia, passing hydrogen sulphide into the alkaline solution and filtering. The phosphorus is then obtained with magnesia mixture as usual. If qualitative tests have shown presence of arsenic the magnesia precipitate is dissolved in hydrochloric acid, arsenic reduced by boiling with sulphurous acid, and precipitated with hydrogen sulphide. In the filtrate the phosphorus is obtained with molybdate, and the yellow precipitate weighed, after collecting on a Gooch crucible with a paper disc.

Arsenic is determined in a separate portion by Lundin's method, just as described by Blair, except that we deem one evaporation to dryness with sulphuric acid sufficient.

In the tin determination, arsenic is separated from the solution of the thiosulphate fusion with magnesia mixture, the tin being then obtained in the filtrate as described.

In the analysis of brass, a more rapid, but not so accurate, determination of the copper and zinc may be obtained by using the iodide method for the former, and the ferrocyanide method for the latter. The foregoing process is carried out to the point of obtaining the filtrate from the lead sulphate. This is mixed with about ten c.c. hydrochloric acid, and the copper precipitated by boiling a few minutes with strips of sheet aluminum. For a neat manner of treating this copper, consult Low's paper already referred to.

The filtrate is ready for titration of zinc with ferrocyanide according to Stone.

The Analysis of White Metal (Antimony being Present).

Proceed as in analysis of bronze up to the point of evaporation with sulphuric acid to remove lead, but in this case use about fifteen c.c. of acid instead of about two. Dilute with eighty-five c.c. water, and filter without unnecessary delay or boiling. Dry and weigh the lead sulphate.

Copper and antimony are thrown down in the solution with hydrogen sulphide, and after boiling the filtrate free from the gas, and oxidising any fine sulphur with nitric acid, zinc is obtained as phosphate in the neutral solution.

The sulphides of copper and antimony are washed from the filter back into the beaker, boiled with a little caustic soda which is passed through the filter, and the filtrate now containing the antimony is added to the solution of the thiosulphate fusion of the nitric acid insoluble residue. The remaining copper sulphide is dissolved by boiling it in 1·20 sp. gr. nitric acid, when it is neutralised and the copper determined with potassium iodide and thiosulphate.

The alkaline solution, containing now all the tin and antimony, is acidulated with hydrochloric acid, and the mixed sulphides filtered out. Ammonium acetate is used for washing as before, but the paper is separated from the dried precipitate and burned alone, followed by the precipitate itself. Ignite in the manner already described for antimony and tin sulphides in the presence of free sulphur. Having obtained the weight of the mixed oxides, it now remains only to determine the antimony, which is attained quite accurately, as follows:—

Grind the residue in the crucible, and pour the powder into a silver crucible containing about six grms. of previously fused caustic potash. Re-weigh the porcelain crucible to ascertain the amount of the residue actually taken for antimony, of course making correction for the difference later.

When fused, dissolve in water, add five grms. tartaric acid, and dilute hydrochloric acid to neutrality. Wash into flask, and add five c.c. strong sulphuric acid and one and a half grms. potassium iodide, keeping the solution down to a bulk of 100 c.c. as nearly as possible. Boil down rapidly to about fifty c.c., observing the precautions already referred to, dilute with boiling water to about 100 c.c., and boil down again to about fifty c.c. The antimony is now all reduced.

Cool, add a pinch of dry phenolphthalein and caustic soda to alkalinity. Discharge the red colour with dilute hydrochloric acid, cool again, add starch paste and fifty c.c. saturated sodium bicarbonate, and titrate with decinormal iodine solution to appearance of the blue colour. We find that by working in this manner one c.c. of the iodine is equivalent to 0·00615 grm. antimony. Theory requires 0·0060.

The tin is obtained by the difference in weight, calculating the antimony to Sb_2O_4. From every 20 per cent tin so obtained, subtract one-tenth per cent, as explained previously.

In conclusion, we may add that any scheme which ignores the antimony passing into the nitric acid solution when the alloy is oxidised, is not worth considering. Working on one grm. it amounts to from three to four per cent of antimony, calculated on the alloy. Some results point to the feasibility of making correction for this solubility, instead of holding back the main precipitate for it.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 20th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Mr. Oscar Guttmann was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. W. M. Bailey, 13, Green Lane Road, New Evington, Leicester; A. J. B. Cooper, Grimstone Lawn, Ealing, W.; John R. Don, D.Sc., M.A., Waitaki, Oamaru, N.Z.; F. W. Dootson, M.A., Bryn, Glisson Road, Cambridge; John Glaister, M.D., 4, Grafton Place, Grafton Square, Glasgow; David Homfray, B.Sc., 6, Dartmouth Row, Greenwich, S.E.; A. F. McEwen, 43, Gilmore Road, Lewisham, S.E.; T. H. Pope, South Street, Ponders End.

Election of Foreign Members.

A ballot for the election of Foreign Members was held, and the following were subsequently declared duly elected:—Professors S. Arrhenius, Th. Curtius, A. P. N. Franchimont, W. Körner, W. Markownikoff, N. A. Menschutkin, H. Moissan, W. Ostwald, F. M. Raoult, I. Remsen, W. Spring, L. J. Troost, P. Waage, J. D. van der Waals.

Announcement by the Council.

The President said that he was authorised by the Council to make the following statement to the Society:—

The Council of The Chemical Society have received the following Memorial and enclosures.

Letter addressed to the Fellows by Messrs. Harden and Hartog.

Owens College, Manchester, October, 1897.

Dear Sir,—We desire to ask if you will give your support to the enclosed Memorial to the Council of The Chemical Society, requesting them to propose such alterations in the Rules of the Society as will enable members who reside in the country to record their votes in the election for officers and members of the Council without personal attendance at the General Meeting.

The reasons for the change which we desire are explained in the Memorial itself, of which a draft is enclosed. That the change is practicable is shown by the fact that in Societies like the Society of Chemical Industry, the Institution of Civil Engineers, and the Institution of Electrical Engineers, each containing several thousand members, the regulations allow votes to be recorded by post, as we suggest, and the arrangements are such that the secrecy of the ballot is preserved. Should you approve of it, we should be much obliged if you would kindly sign and return the draft Memorial under cover to one of the undersigned at your early convenience.

We are, dear Sir,
Faithfully yours,
Arthur Harden.
Philip Hartog.

Memorial.

To the President and Council of The Chemical Society.

Gentlemen,—We the undersigned, Fellows of The Chemical Society, desire to draw your attention to the great change in constitution which has taken place since the Society was originally formed, and to the desirability of making some alteration in the Bye-laws, so as to correspond with this change. Whereas the Society was originally composed in the main of chemists living in London or its immediate neighbourhood, and until 1871 was called on its official publication The Chemical Society of London, since that date it has been called by the more general name (given in the Charter) of The Chemical Society, and at the present time the vast majority of the Fellows reside in other parts of the kingdom.

Under the existing regulations it is, however, practically impossible for this majority to take any share in the government of the Society, since, under Bye-law V., the vote of each member at the election of Officers and Council must be recorded *personally*, and may not be sent by post.

It is, of course, recognised that a custom has grown up of choosing a certain proportion of the Officers and Council from among the Fellows who reside in the provinces, but this practice cannot be regarded as a sufficient remedy for the defect in the existing Bye-law, and while we do not wish in any way to express dissatisfaction with the policy of the present or of past Councils, we feel strongly that the Council should be elected by the whole Society, and not by a mere fraction of the Fellows. In this feeling we venture to think that you will concur.

We trust, therefore, that you will see your way to propose to the Society at an early date an alteration of Bye-law V. in the sense we desire, and have the honour to remain, Gentlemen,

Your obedient Servants,
(Signed by 540 Fellows).

Letter received by the Secretaries, together with the Memorial and Enclosures.

Owens College, Manchester, December 16th, 1897.

Gentlemen,—We beg to forward herewith a Memorial addressed to the President and Council of The Chemical Society, together with the signatures of over 500 Fellows appended thereto. We also enclose a list of the signatures divided into two sections:—(*a*) A list of the signatures appended to the Memorial in the first instance—*i.e.*, before it was circulated among the Fellows of the Society residing in the United Kingdom generally; (*b*) a list of signatures appended subsequently. With reference to the substance of the Memorial we wish to make one statement. We are aware that in the Charter (on page 8 of the printed text) it is provided that "at all general meetings and meetings of the Council, the majority present, and having the right to vote thereat respectively, shall decide upon the matters propounded at such meetings"; hence in order to render legal the change desired, it would probably be necessary to obtain a Supplemental Charter, allowing members not actually present at meetings to vote by means of balloting papers. It is in this connection material to point out that in order to obtain a revision of Bye-laws precisely similar to that now desired by Fellows of our own Society, a supplemental Charter was quite recently obtained by the Institution of Civil Engineers. We beg to request you to lay the accompanying Memorial and enclosures, and the present letter, before the President and Council of The Chemical Society, and have the honour to remain, Gentlemen,

Your obedient Servants,
Arthur Harden.
Philip Hartog.

The Secretaries of The Chemical Society.

Owing to the action of the Bye-laws Committee, which was appointed some time ago, the Council is in a position to give an immediate answer to the Memorialists.

The question of the power of the Society to alter the mode of election of the Officers and Council having arisen, the Bye-laws Committee requested the solicitors of the Society, Messrs. Wilson, Bristows, and Carpmael, to submit the following case for legal opinion:—

Case for the Opinion of Counsel.

The opinion of Counsel is desired by the President and Council of The Chemical Society under the following circumstances:—

A memorial is being extensively signed by the Fellows of The Chemical Society, addressed to the President and Council of such Society, asking that the Bye-laws may be altered so as to allow the votes at the General Annual Meetings to be given by proxy. A printed copy of such Memorial is sent herewith.

The attention of Counsel is directed to page 8 of the printed copy of the Charter of The Chemical Society, which is sent herewith, and also to pages 16 and 17 of such document. On the latter of which pages will be found the present Bye-laws on the subject.

Counsel is desired to advise the President and Council of The Chemical Society whether, under their Charter, they have power to alter the Bye-laws so as to provide for the votes at General Meetings being given by proxy.

The following is the opinion of Counsel:—

Copy of Opinion of Mr. Cozens-Hardy, Q.C.

I am of opinion that the Charter (p. 8) prohibits voting by proxy, and that any Bye-law framed for the purpose of allowing voting by proxy would be repugnant to the Charter (p. 9) and invalid.

Herbert H. Cozens-Hardy.

7, New Square, Lincoln's Inn,
December 6, 1897.

This opinion of Mr. Cozens-Hardy, Q.C., makes it clear that the Council of the Society have not the power to propose such an alteration of Bye-law V. as the Memorialists request.

The suggestion made by Messrs. Harden and Hartog in the letter addressed to the Secretaries along with the Memorial, that "*it would probably be necessary to obtain a Supplementary Charter allowing members not actually*

present at meetings to vote by means of balloting papers," opens up questions outside the terms of the Memorial, which will necessitate further legal advice. The whole subject is receiving the most careful consideration of the Council.

Of the following papers those marked * were read:—

*1. "*The Preparation of Pure Iodine.*" By BEVAN LEAN, D.Sc., B.A., and W. H. WHATMOUGH.

Stas, in his "Nouvelles Recherches sur les Lois des Proportions Chimiques," states that he was only able to find two methods of preparing iodine free from chlorine and bromine. One consisted in precipitating by water iodine dissolved in potassium iodide, the other depended on the decompositions of iodide of nitrogen by heat. Perhaps the main difficulty attached to these methods was the desiccation of the iodine and the removal of hydriodic acid. Neither in his published memoirs nor in his laboratory note-books has Stas stated how he assured himself that his "iodine" was free from other halogens.

A few months ago the authors observed incidentally that no iodine is set free when cuprous iodide is heated, even at its fusion-point, in a current of carbonic anhydride, although it is readily evolved when cuprous iodide is heated in air, oxygen, nitric oxide, or nitrogen peroxide. The action is represented by the equation $Cu_2I_2+O_2=2CuO+I_2$. No iodine is evolved when cuprous iodide is heated in a vacuum.

The authors have examined the usual methods of preparing cuprous iodide. When a solution of cupric sulphate and a soluble chloride, bromide, or iodide is saturated with a sulphurous acid, cuprous iodide, bromide, and chloride may all be precipitated; but there is so great a difference in their degree of solubility that, by securing a proper dilution, it is probable that cuprous iodide can be prepared free from cuprous bromide or chloride. A mixture of cupric sulphate and ferrous sulphate is still less liable to precipitate cuprous bromide and chloride along with cuprous iodide than cupric sulphate saturated with sulphurous acid. The authors have found that cuprous iodide can also be prepared by sprinkling iodoform in small quantities at a time upon a hot surface of copper. On account of the difference in the properties of chloroform, bromoform, and iodoform, it is probable that, by this method also, cuprous iodide can be prepared entirely free from bromide or chloride. If, moreover, the cuprous iodide is fused in a current of carbonic anhydride, or *in vacuo*, it can be freed completely from moisture.

Iodine is most conveniently prepared from cuprous iodide by heating it in a stream of dry air at 220° to 240° and condensing the vapours upon a cold surface. Although the greater portion of the iodine in a given quantity of cuprous iodide is quickly expelled, it is not easy to expel the whole; after heating 1·7101 grms. at 400° for eighteen hours, 0·15 per cent of the iodide was still undecomposed—otherwise the relation Cu_2I_2:2CuO could have been utilised for the exact measurement of the atomic weights of copper, iodine, and oxygen. The authors are making further experiments upon this point. The action of air upon cuprous iodide is not dependent upon the presence of moisture. This is established by sealing cuprous iodide in glass tubes in the presence of phosphoric anhydride.

Iodine liberated as described from cuprous iodide at 240° leaves absolutely no residue when volatilised at 75°. If examined spectroscopically, no evidence of the presence of copper can be found. The melting-point (uncorrected) is 112·5° to 114°.

Whether such iodine is as pure as that prepared by Stas or not, it appears desirable to re-determine the atomic weight of the element prepared by this method.

DISCUSSION.

Dr. SCOTT remarked that Stas depended on distillation two or three times with anhydrous baryta, and not on calcium nitrate, for the complete removal of water from his iodine. This reagent had also the great advantage of removing any traces of hydriodic acid, the calcium nitrate being only used for the removal of the greater part of the water. Although Stas does not give his methods of testing his iodine for traces of chlorine and bromine, his concluding remarks in that section of his paper evidently show that he had no doubts as to its purity. The marvellous agreement of his results with those of Marignac, who found 100 grms. of silver gave 217·5334 of silver iodide, whilst Stas found in his complete synthesis 217·5335, will probably convince most chemists that both were dealing with the same chemical substance.

Mr. R. J. FRISWELL asked if the author had observed the crystalline form and appearance of the sublimed iodine. He had himself a very interesting experience in this matter with iodine recovered from methyl iodide by Nicholson's method of recovering the iodine, used in methylating rosaniline by mixing the sulphuric acid and sodium bichromate with the waste iodine liquor, the precipitated iodine being washed, pressed, and fused under sulphuric acid.

For many years he (Mr. Friswell) had noticed that at times the sulphuric acid used for the fusion contained a mass of minute, violet-brown, glistening plates, but every attempt to collect them failed, the least dilution of the acid causing them instantly to disappear. After some time, however, nearly a pound of a paste or magma of these crystals was obtained in the following way:—The acid was allowed to dilute itself by the absorption of water from the air and then run off from the crystals; the magma of crystals was thrown on to a vacuum filter and washed with sulphuric acid of continually increasing dilution, and at length with water; the paste was then squeezed, and, while moist, sublimed in a beaker covered with a loose glass plate at a temperature of 35 to 40°.

At first, the ordinary violet plates of iodine appeared, with a little water, but these soon vanished, and intensely black, adamantine, solid rhombic (?) crystals appeared. A brownish earthy residue was left. The crystals were of considerable size, a cubic m.m. or so in content. He thought that since these had been obtained from iodine continually in use for many years, during which time some tons of iodine had passed through the operation, they might be the companion element which has been suspected. Prof. Ramsay was asked to examine the crystals and the paste from which they had been sublimed, but found that the adamantine crystals gave no residue on sublimation and showed 99·84 per cent iodine, the deficit being probably due to a slight accidental loss. On sublimation in a vacuum, both the plate-like crystals which first sublimed and iodine purified in the usual way left slight yellowish residues, but these adamantine crystals left none. They were, therefore, pure iodine. He wished to know whether the author's substance resembled these crystals in any way.

The PRESIDENT mentioned, as indicating the general trustworthiness of Stas's observations, that he had recently confirmed Stas's remarkable statement, that, when pure, solid iodine is opaque to light. He inquired whether Dr. Lean had made any experiments with palladious iodide.

Dr. LEAN, in reply, said that he had not noticed anything anomalous in the crystallisation of the iodide. He had observed, however, that his iodine had a black and not a deep violet colour, and that it emitted no visible vapour at the ordinary temperature. Stas had made a similar observation.

The reason he had not made most of his experiments with palladious iodide was that it was so much more expensive than cuprous iodide. He had, however, made a few experiments which showed that iodine was very readily liberated when palladious iodide was heated in air.

*2. "*Derivatives of Bromtolylhydrazine.*" By J. T. HEWITT, M.A., D.Sc., and F. G. POPE.

This is a continuation of the work of one of the authors on ortho-substituted phenylhydrazines. The hydrazine was prepared from the amido-compound by the

method of Victor Meyer and Lecco (*Ber.*, 1883, xvi., 2976), an alteration being made by pouring the solution of the diazonium salt into the stannous chloride solution. The free hydrazine and the following salts and derivatives are described:—

Bromtolylhydrazine, $C_6H_3BrMe(N_2H_3)$, 1 : 3 : 6, colourless needles, m.p. 91°; *hydrochloride*, $C_7H_6Br\cdot N_2H_3,HCl$, colourless needles, m. p. 190°; *nitrate*,—

$$C_7H_6Br\cdot N_2H_3,HNO_3,$$

colourless plates, m. p. 154°,; *sulphate*,—

$$(C_7H_6Br\cdot N_2H_3)_2,H_2SO_4,$$

colourless needles, m.p. 201°; *oxalate*,—

$$(C_7H_6Br\cdot N_2H_3)_2,\ H_2C_2O_4,$$

small colourless prisms, m.p. about 150°. *Acetylbromtolylhydrazine*, $C_7H_6Br\cdot NH\cdot NH\cdot COMe$, colourless prisms, m. p. 124°. *Bromtolylsemicarbazide*,—

$$C_7H_6Br\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

small colourless crystals, m.p. 163°. *Bromtolylallylthiosemicarbazide*, $C_7H_6Br\cdot NH\cdot NH\cdot CS\cdot NH\cdot C_3H_5$, colourless prisms, m.p. 136·5°. *Bromtolylphenylthiosemicarbazide*, $C_7H_6Br\cdot NH\cdot NH\cdot CS\cdot NH\cdot C_6H_5$, small prisms often grouped in radiating clusters, m.p. 142°; the freshly-prepared substance usually has a somewhat lower melting-point, and this may possibly be a case of isomerism similar to that observed by Marckwald with diphenylthiosemicarbazide (*Ber.*, 1892, xxv., 3098). *Furfuraldehydebromtolylhydrazone*,—

$$C_4H_3O\cdot CH:N_2H\cdot C_7H_6Br,$$

needles, m. p. 87°. *Benzaldehydebromtolylhydrazone*, $C_6H_5\cdot CH:N_2H\cdot C_7H_6Br$, rhomboidal plates, m.p. 84°. *Salicylaldehydebromtolylhydrazone*,—

$$C_6H_4(OH)\cdot CH:N_2H\cdot C_7H_6Br,$$

needles, m.p. 109°, and the following bromtolyl hydrazones of:—*pyruvic acid*, $C_7H_6Br\cdot NH\cdot N:CMeCO_2H$, yellow crystals, m.p. 175°; *ethyl pyruvate*,—

$$C_7H_6Br\cdot NH\cdot N:CMeCO_2Et,$$

tufts of needles, m.p. 84—85°; *potassium pyruvate* (with 3 mols. of water), $C_7H_6Br\cdot NH\cdot N:CMeCO_2K,3H_2O$; *ammonium pyruvate*, $C_7H_6Br\cdot NH\cdot N:CMeCO_2NH_4$ (both these salts are soluble in hot water, sparingly, however, in cold water); *lead pyruvate*,—

$$[C_7H_6Br\cdot NH\cdot N:CMeCO_2]_2Pb,$$

a pale yellow precipitate.

The effect of heat on the potassium and lead salts is to furnish potassium or lead bromide as well as basic and acidic or phenolic decomposition products. The reactions are being further examined.

*3. "*Researches on the Terpenes.* I. *On the Oxidation of Fenchene.*" By John Addyman Gardner and George Bertram Cockburn.

The authors give an account of their method of producing fenchene from fenchone, the oxidation products of fenchene, and pinene hydrochloride.

Fenchone, b.p. 191—192°, m.p. 6°, specific rotatory power $[\alpha] = +61°\ 58'$ was reduced to fenchyl alcohol by a modification of Wallach's method, using amyl alcohol and sodium instead of ethyl alcohol and sodium. It was obtained in hard, white crystals, m.p. 45°, specific rotatory power $[\alpha] = -13°\ 38'$.

The fenchyl alcohol was converted into fenchyl chloride by the action of phosphorus pentachloride, and this into fenchene by saponification with aniline. The bulk of the fenchene thus obtained distilled for the most part between 150° and 156°, several degrees lower than that described by Wallach, which boiled between 158° and 160°. A fraction, 152—154°, was shown by combustion to have the formula $C_{10}H_{16}$. Its specific gravity was 0·8667 at 18°, and specific rotatory power $[\alpha] = -6°\ 46'$ (not in solution). The specific gravity of Wallach's hydrocarbon was 0·864 at 20°, and it was optically inactive.

As a by-product in the action of fenchyl chloride on aniline, the authors obtained a black oil, not volatile in steam. This substance did not solidify on standing, but on distillation under reduced pressure came over for the most part at 171—173° at 13 m.m. pressure. It was a pale yellow, thick, viscous oil, which turned black on exposure to air. Analysis showed it to have the composition $C_{10}H_{17}NHC_6H_5$. On treatment with acetyl chloride it yielded a thick, viscous oil, of the composition—

$$C_{10}H_{17}N(Ph)COMe.$$

Fenchene was oxidised by heating it on the water-bath with nitric acid (1 nitric acid : 1 water). When the oxidation was complete the liquid was distilled in steam, when some acetic acid was obtained. The residue was then evaporated to small bulk, and on standing crystals of cis-camphopyric acid separated out. After the removal of these crystals, the oily mother-liquors were eventually distilled *in vacuo*. An acid oil and a neutral solid distilled over; these were separated by means of sodium carbonate, and the solid crystallised from alcohol. It proved to be camphopyric anhydride, m.p. 178°. The yield of camphopyric acid obtained in these experiments was about 20 per cent.

Turpentine hydrochloride was heated on the water-bath with nitric acid (2 nitric : 1 water). The oxidation was exceedingly slow, but after about ten days the bulk of the hydrochloride had disappeared. The greater part of the acid was then distilled, and contained a considerable proportion of acetic acid. The residue was then evaporated to complete dryness, dissolved in ether, and the ethereal solution extracted with sodium carbonate.

The acids extracted by the alkali were converted into insoluble lead salts. The lead salts were decomposed by sulphuric acid, and extracted with ether. On evaporating the ether an oil was obtained which, on standing, deposited crystals of camphoric acid; the purified acid melted at 202—203°, and its anhydride at 217°.

The oil left after separation of these crystals was distilled in a vacuum; an oil distilled over between 120—130°, a smaller portion at 130—150°, and a considerable amount at 180—200°, which solidified on standing. This latter portion was purified by sublimation and crystallisation from alcohol, and proved to be camphopyric anhydride, m. p. 178°.

The yield of camphoric acid from 300 grms. of turpentine hydrochloride was 18 grms., and of camphopyric anhydride 8—9 grms. The authors were unable to isolate any camphoic acid.

4. "*The Action of Alkalis on Amides.*" By Julius B. Cohen, Ph.D., and Charles E. Brittain, B.Sc.

The authors have succeeded in preparing a series of compounds of the general formula, $R'NH\cdot C_2H_3O\cdot NaOH$ and $R'NHC_2H_3O\cdot KOH$, by the action of the caustic alkalis on amides under certain conditions. These substances are analogous in their mode of formation, and in properties to the alcoholates previously described (Cohen and Archdeacon, *Trans.*, 1896, lxix., 9), and probably possess a similar constitution, which may be expressed by the formula—

$$\begin{array}{l} R'—N—Na \\ \quad\quad | \\ Me\cdot C{<}^{OH}_{OH}. \end{array}$$

5. "*The Formation of Monomethylaniline from Dimethylaniline.*" By Julius B. Cohen, Ph.D., and Harry T. Calvert, B.Sc.

When phenylnitrocarbinol (*Trans.*, 1897, lxxi., 1050) acts on dimethylaniline a violent reaction occurs, and the dimethylaniline is converted into nitrosomethylaniline, and at the same time nitrogen is evolved, and benzylalcohol and benzaldehyd are formed. As phenylnitrocarbinol readily evolves nitrous fumes on standing, and reacts in some cases like nitrous acid, this result suggested the possibility of a similar reaction occurring when nitrogen trioxide acts upon dimethylaniline. The latter action

is, however, entirely distinct from that of phenylnitrocarbinol or nitrous acid, and will form the subject of a future communication.

6. "*Note on the Aluminium-Mercury Couple.*" By Julius Cohen, Ph.D., and Harry T. Calvert, B.Sc.

The authors find that when aluminium is amalgamated with mercuric chloride, a small quantity of chlorine is retained by the aluminium, and is probably present as oxychloride. The presence of the chlorine first became evident in the process of reducing a nitro-compound in neutral solution, when, instead of the free base, the hydrochloride was formed.

7. "*Action of Chloroform and Alkaline Hydroxides on the Nitrobenzoic Acids.*" By Walter J. Elliott, M.A.

The author finds that the meta- and para-acids are reduced to the corresponding azoxy-acids, while the ortho-acid is not appreciably affected.

PHYSICAL SOCIETY.

Ordinary Meeting, January 21st, 1898.

Mr. Shelford Bidwell, President, in the Chair.

Prof. Fitzgerald exhibited some photographs by Mr. Preston, in illustration of the Zeeman effect, for various cases, including those of iron, cadmium, zinc, and sodium. These photographs and the method of obtaining them have already been described. The cause of doubling is now attributed by Prof. Fitzgerald to absorption by the surrounding vapour. In a particular case he examined a double line that exists in one of the photographs. Under the polariser the two lines are at first distinctly seen; but when the polariser is turned a thin line appears in the middle, and this central line is therefore circularly polarised in a direction opposite to that of the outer pair of lines. The reason for the appearance of doubling in the first position of the polariser is, that the central line is there completely absorbed out by the surrounding vapour.

Prof. Oliver Lodge then gave a communication concerning his work on "*Electric Signalling without Connecting-Wires.*"

From the nature of the oscillatory disturbances emanating from any of the customary forms of Hertz vibrator, syntony has hitherto been only very partially available as a means for discriminating between receivers. There is, in fact, so rapid a decrease in the amplitude of the vibrations that almost any receiver can respond to some extent. Discrimination by syntony is possible with magnetic systems of space telegraphy, where the magnetic energy much exceeds the electric, *i.e.*, as between two separated inductive coils; and by the use of such coils, appropriately applied, the author has been able to attain fair syntony even with true Hertz waves,—*i.e.*, he has constructed spark-gap oscillators, with sufficient persistence of vibration, and syntonised resonators. The "coherer" principle can be applied to either a purely magnetic or to the Hertzian system. It was first used by Prof. Lodge in devising lightning-guards, and afterwards in his magnetic system of telegraphy by inductive circuits, each in series with a Leyden jar; a pair of knobs in near contact, or other over-flow gap, being provided in the receiving apparatus. This was the first meaning of a "coherer" in the electrical sense as used by Prof. Lodge: it referred to a *single* contact between two metal knobs. The term has since been extended by others to the filings-tube of M. Branly, and some confusion has arisen, for M. Branly does not consider that simple coherence and break explains fully the behaviour of his instrument. Prof. Lodge is disposed to agree, for he finds that the resistance of almost any form of coherer varies in rough proportion to the received impulses, and that there are other peculiarities (to be mentioned later); he is therefore inclined to think that the action cannot after all be entirely explained as due to mere "welding," but that there is something more to be learnt about it. The sensitiveness of a coherer depends upon the number of loose contacts; it is a maximum for a single contact, *i.e.*, for a needle-point lightly touching a steel spring. With this sensitive coherer, hardly any "tapping-back" is required for decoherence, but it wants delicate treatment when properly adjusted, and the greatest current through it should not approach a milliampère. On the other hand, a Branly tube rather improves under rough treatment; in such a tube the author prefers to use iron filings in the best possible vacuum: brass, too, is very good, but rather less easy to manage. Aluminium is thoroughly bad, and gold, for an opposite reason, will not work—its surface is too clean. Points, or small surfaces for making contact with the filings, are better than large surfaces. The usual method of connecting the coherer across the gap of an ordinary Hertz receiver, in parallel with the telegraph instrument and battery, has the unavoidable objection that they shunt away part of the received oscillations. With the syntonic receiver of Prof. Lodge, which contains no gap, but a closed wire coil instead, the difficulty no longer exists; for the coherer can now be in series with the detecting instrument, and, in so far as these obstruct the oscillations, they may be shunted out in various ways, as the author describes. The main feature of his new syntonised vibrators is this self-inductance coil, whose function it is to prolong the duration of the oscillations, and thereby to render syntony possible. Although such a coil acts disadvantageouly in so far as it possesses resistance, the resistance does not increase so fast as the self-induction. The coil should consist of thick copper of highest conductivity, and it should have maximum inductance for given resistance. For similar reasons, the capacity areas should also be of highest conductivity, their dimensions should increase outwards from the spark-gap, as triangles. The receiver must have no gap, it should be accurately bridged over when a transmitter is used as receiver. The limit of speed of response depends upon the telegraphic instrument. Dr. Muirhead adapted a syphon-recorder to the purpose, because it is one of the quickest responders; he arranged it so that it could be used with intermittent currents, direct. Under these intermittent impulses the syphon trembles, and instead of the ordinary syphon-signals, the slip is marked with dots and dashes. Constant mechanical tremor is usually employed for decoherence, but the author finds that decoherence can be brought about by electrical means, without any mechanical tremor, by connecting the coherer momentarily to a circuit less effective as a collector than that of the proper capacity areas of the syntonised receiver. The battery and galvanometer detector-circuit may be used for this purpose, the coherer being momentarily connected to it, and while so connected letting it experience an impulse from a distance. Prof. Lodge has designed a revolving commutator, by means of which the coherer can be rapidly changed over from the resonating circuit to the instrument circuit, and finally to the "tapping-back" apparatus. A coherer is more sensitive when thus isolated and exposed to the full influence of the received oscillations; the subsequent detection of the effect by altered connections is very convenient for laboratory measurements. A diagram of a series of plotted measurements showed that the resistance of an undisturbed filings-tube is approximately a direct function of the intensity of the received stimulus, whether successive stimuli increased or decreased in strength. This electrical process of "tapping back" is to be depended upon, but the process long continued fatigues the tube until a mechanical shake is employed to restore it. Large size apparatus, made by Dr. Muirhead for actual

distant syntonic work, was exhibited, and means were shown for protecting and isolating the coherer when its receiving areas were being used as emitters; also a switch used for changing at one movement all the connections from "sending" to "receiving."

Prof. THRELFALL said he had come to the same conclusion as Prof. Lodge as to the advisability of diminishing the number of contact points in the coherer. He had endeavoured to produce longer and more persistent waves, and thus to set afield greater effective energy. It was desirable to keep the waves as parallel as possible. He thought there was some probability that the wave-fronts could be altered and rendered more comformable by a process of diffraction.

Mr. RUTHERFORD also had found it best to work with long waves. He fully appreciated the advantage of increasing the capacity of the oscillator by extending the surface of the metallic plates.

Mr. CAMPBELL-SWINTON asked whether experiments had been made to verify Hertz's results as to the influence of reflectors behind oscillators and receivers. He had found them disadvantageous. A single wire behind either apparatus seemed partially to annul the effect. He also asked whether Prof. Lodge had observed the extraordinary sensitiveness of coherers to small changes of current in neighbouring circuits.

Prof. LODGE, in reply, said he had observed the sensitiveness to slight sudden variations of current referred to by Mr. Campbell-Swinton; for instance, when electric lamps were switched on and off. The effect of mirrors had been studied by Prof. Fitzgerald. They required to be of large dimensions as compared to the oscillator and receiver, otherwise the true reflections were not obtained.

Dr. SILVANUS THOMPSON afterwards exhibited a Tesla Oscillator. This apparatus is intended to replace the two induction coils and spark-gap arrangements used by Mr. Tesla for high frequency experiments. It consists of an induction coil, with a separate self-inductance coil in the primary circuit. This self-inductance coil is also used as an electromagnet for the separate interrupter of the primary circuit. A condenser is connected between one end of the primary coil and one terminal of the interrupter, so as to include both of them between its terminals. The primary is a single turn of copper strip six inches wide. The secondary is one layer of thick wire, each turn separated from the next by an air space. The supply current, about half an ampère, may be taken from the electric light mains at almost any voltage from 50 to 200, direct or alternating.

Prof. LODGE said it would work quite well at 10 volts. He pointed out also that if the straight discharge rods at the spark-gap were free to slide, the discharge drove them back into their sockets.

Prof. FITZGERALD said it was stated at Toronto that the spark was broken at the interrupter when the condenser was charged, and that by the time the condenser was ready to discharge, the contact at the interrupter had been made again. It seemed to him that the condenser discharges and surgings must take place at a rate far higher than the period of the mechanical movement of the interrupter. The condenser charges and discharges were very rapid. It was not what is ordinarily called the "time constant" that was involved, for that only referred to constant voltage. Here the voltage was changing very rapidly indeed.

Prof. HERSCHEL asked if such an apparatus was suitable for work with Röntgen rays.

Dr. THOMPSON, in reply, congratulated Mr. Tesla upon the perfect working and compactness of his invention. The present form was not suited for Röntgen ray experiments, but Mr. Tesla had designed a special coil that was excellent for that purpose.

The PRESIDENT proposed votes of thanks, and the meeting was adjourned until February 11th.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 1, January 3, 1898.

M. van Tieghem was elected Vice-President for the year 1898.

MM. Darboux and Bornet were elected members of the Central Administrative Committee for 1898.

The retiring President, M. Ad. Chatin, announced the condition of the publications of the Académie, and the changes which have taken place among the members during the year 1897.

On the Isocyanic Ethers, and the Heat of Formation of Liquid Cyanic Acid.—Paul Lemoult.—Isocyanates obtained by the action of methyl and ethyl sulphuric ethers on cyanate of potassium give but a small return. A better way is to heat cyanate of potassium with ethylsulphate of soda; the liquid produced contains 15 per cent of pure isocyanate of ethyl. *Isocyanate of methyl* is a colourless liquid boiling at 40° and polymerising with great facility. The results of some calorimetric experiments were—Heat of combustion of 1 grm., 4718·1 cals., 4732·3 cals., 4705·4 cals.; average, 4718·6 cals. From this is deduced:—

	Heat of molecular combustion.	Heat of molecular formation.
At constant volume ..	268·9 cals.	
At constant pressure ..	269·3 ,,	+22·8 cals.

Isocyanate of ethyl boils at 60°, and is much more stable than the above; calorimetric experiments give—

	Heat of molecular combustion.	Heat of molecular formation.
At constant volume ..	424·2 cals.	
At constant pressure ..	424·4 ,,	+31 cals.

From the above results the author deduces that the heat of formation of liquid cyanic acid is +20·8 cals.

A New Cyclic Ketone, Methylcyclohexenone.—A. Behal.—Methylcyclohexenone reacts on perchloride of phosphorus with considerable disengagement of heat, and forms an intensely blue-green liquid, soluble in alcohol; it becomes brown on the addition of water and alkalis; its oxidation by means of permanganate is very decided—nothing but acetic and levulic acids are formed.

No. 2, January 10, 1898.

This number contains M. Chatin's farewell address, and a long list of prizes proposed and to be awarded, but there is nothing suitable for useful abstraction.

MISCELLANEOUS.

A Simple and Efficient Boiling-point Apparatus for Use with Low- and with High-boiling Solvents.—Harry C. Jones.—The author discusses the various forms of apparatus in use, and suggests a modification of Hite's apparatus, in which the condensed solvent is not returned directly into the boiling solution. The apparatus consists of a tube about one-fourth filled with glass beads, on which rests a platinum cylinder. The thermometer is immersed in the solvent inside the cylinder, which serves to separate the condensed solvent and boiling solution. The results obtained seem to be very satisfactory.—*Journal of the American Chemical Society*, xix., No. 12.

MEETINGS FOR THE WEEK.

Monday, 7th.—Society of Arts, 8. (Cantor Lectures). "Decorative Bookbinding," by Cyril Davenport.
— Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "The Curing of Malt in Relation to Colour and Value," by J. W. Lovibond. "Clerget's Method of Estimating Cane-sugar," by A. R. Ling. "A New Modification of Clerget's Method of Estimating Cane-sugar, specially applicable to Molasses and After Products," by A. R. Ling and J. T. Baker. "Note on the Estimation of Water in Invert Sugars," by Dr. L. T. Thorne and E. H. Jeffers.
Tuesday, 8th.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LLD., F.R.S.
Wednesday, 9th.—Society of Arts, 8. "Compensation to Workmen," by A. D. Provand, M.P.
Thursday, 10th.—Royal Institution, 3. "Some Italian Pictures at the National Gallery," by Jean Paul Richter.
Friday, 11th.—Physical, 5. (Annual General Meeting). President's Address. "On Electromagnetic Induction in Plane, Cylindrical, and Spherical Current Sheets, and its Representation by Moving Trails of Images," by G. H. Bryan, M.A., F.R.S.
— Royal Institution, 9. "The Metals Used by the Great Nations of Antiquity," by J. H. Gladstone, Ph.D., D.Sc., F.R.S.
Saturday, 12th.—Royal Institution, 3. "The Structure of Instrumental Music" (with Musical Illustrations), by William H. Hadow, M.A., B.Mus.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Dyers' Journals.—Would any correspondent kindly oblige me with the addresses of the publishers of the leading "dyers' journals" of Germany and Italy.—J. L.

TO CORRESPONDENTS.

J. E. Morce.—The only available information is to be obtained in Prof. Dewar's papers read before the Royal Society, and his lectures at the Royal Institution.

McGILL UNIVERSITY, MONTREAL.

CHAIR OF CHEMISTRY.

The Board of Governors is prepared to receive applications for the additional Chair of Chemistry newly instituted by Mr. W. C. McDonald. Candidates should produce evidence of special qualifications in Organic Chemistry.

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THE CHEMICAL NEWS.

VOL. LXXVII., No. 1994.

THE HOMOGENEITY OF HELIUM.*

By WILLIAM RAMSAY, Ph.D., LL.D., Sc.D., F.R.S., and MORRIS W. TRAVERS, B.Sc.

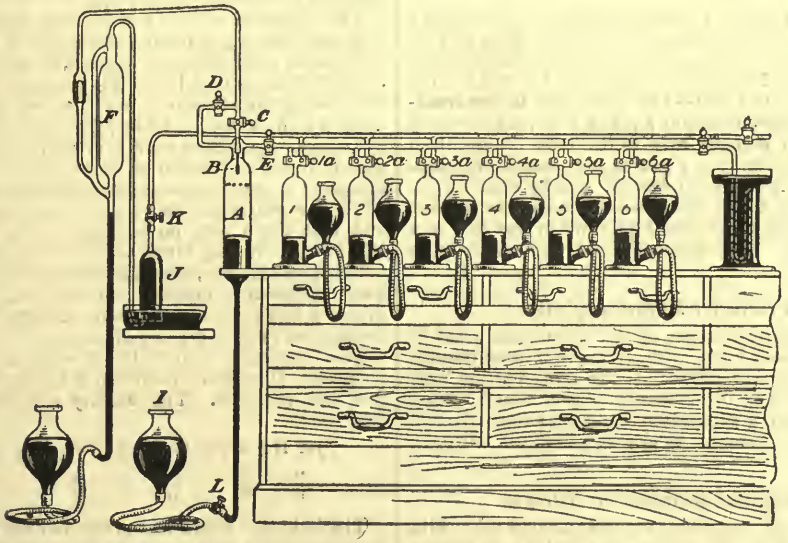
ABOUT a year ago, a paper by Dr. Norman Collie and one of the authors (W. R.) was published, bearing the title "The Homogeneity of Helium and of Argon." In that paper (*Roy. Soc. Proc.*, lx., p. 206) various reasons were adduced to show why an attempt to determine whether or no argon and helium are homogeneous was worth making. The results of the experiments at that time indicated that, while it did not appear possible to separate argon into two portions of different densities, the case was different with helium. Samples were obtained after repeated diffusion which possessed respectively diffusion rates corresponding to the densities 2·133 and 1·874. It was there pointed out that these densities are not correct (although their ratio is probably not wrong), owing to the curious fact that the rate of diffusion of helium is too rapid for its density, *i.e.*, it does not follow Graham's law of the inverse square root of the densities. These samples of gas also differed in refractivity, and the difference was approximately proportional to the difference in density.

Towards the end of the paper, the conjecture was hazarded that it was not beyond the bounds of possibility that the systematic diffusion of what we are accustomed to regard as a homogeneous gas—for example, nitrogen—might conceivably sift light molecules from heavy molecules. It is true that the fineness of the lines of the spectrum would offer an argument in favour of the uniformity of molecular weight; but still it is never advisable to assume any physical theory without submitting it to rigorous proof. And it was thought possible that the fractional diffusion to which helium had been subjected might have had the result of effecting such a separation,—a separation, not of chemical species, but of molecular magnitude. The other and more ordinary explanation of the splitting of helium into fractions of different density is that helium must be regarded as a mixture of two gases, one lighter than the other.

Since the publication of the paper mentioned, Dr. A. Hagenbach has confirmed the possibility of separating helium into portions of two densities by diffusion; and the differences in density were practically the same as those observed in the laboratory of University College (*Wied. Ann.*, lx., p. 124).

These experiments were made with somewhat over 200 c.c. of gas; but it was decided to make experiments of a similar kind on a much larger quantity of helium.

An apparatus was therefore constructed, similar in principle to the one previously employed, but on a much larger scale. The main features are shown in the illustration on p. 208 of the paper previously alluded to; but on account of the large amount of gas diffused, it was not practicable to collect it in tubes. Instead, therefore, of the bent tube E N of the former apparatus, the tube connected with the stopcock E was continued horizontally, and by means of six vertical branches it communicated with six gas reservoirs, each furnished with a two-way stopcock. It was possible with this means to cause gas



from any one of the reservoirs to enter the diffusion apparatus A. In order to be able to collect the gas in any desired reservoir, the delivery tube of the Töpler pump, F, delivered gas into a jar somewhat similar to that shown at J, but provided with a vertical branch, which was bent horizontally some distance up, and lay parallel to the previously mentioned horizontal tube. It, too, had six vertical branches, each of which communicated with the other limb of the two-way stopcock of each reservoir. By raising the reservoir of the Töpler pump and expelling gas into the collecting tube J, the gas could be transferred to any one of the reservoirs. The accompanying diagram makes it clear how the apparatus was set up.

The actual method of conducting a diffusion was as follows:—

Reservoir 1 was raised until the mercury in the diffusiou jar A stood at the level of the dotted line. The clip I. was then closed, and the stopcocks C and D opened. The Töpler pump was then worked until all gas was removed from A; the gas, if air (as at the commencement of the whole series of operations), being allowed to escape by moving the collecting jar J, so that it no longer covered the end of the exit tube of the Töpler pump. Stopcocks C and D were next closed, and stopcocks E and 6*a* opened,

* A Paper read before the Royal Society, January 20th, 1898.

so that the gas from 6 entered the diffusion vessel A. By raising the reservoir belonging to 6, all gas was expelled through E into A, clip L being opened meanwhile. Reservoir 6 was now full of mercury, and all gas was in A. Stopcock C was then opened, and the gas in A diffused through the pipe-stem B (closed at one end by means of an oxyhydrogen blowpipe) into the pump. This diffusion proceeded until half the gas in A had passed into the pump reservoir F. Stopcock C was then closed, and the Töpler was worked, the diffused gas being delivered into J. Stopcock 6*a* was then opened, and the reservoir of 6 lowered, so that the gas in J passed into 6. This stopcock was then shut. The contents of 5 were then transferred in a similar manner into A, and one-third of the gas was diffused into the pump. It was collected as before in 6. The diffusion jar A now contained as much gas as had been present in 5. The contents of 4 were next added; half of this was removed by diffusion and transferred to 5. The contents of 3 were added; half was diffused and transferred to 4. The contents of 2 were added; half was diffused and collected in 3. And, lastly, the contents of 1 were added, and the halt diffused collected in 2. Stopcock D was then opened, and the mercury in the diffusion jar A allowed to run up to the dotted line; the clip L was closed. All gas was pumped out of A and collected in 1; this constituted one complete round.

As it was not possible to empty the tube issuing from J completely of gas by lowering the reservoir of 1, and as, if not emptied, the heavy gas would have contaminated the light gas from 6 during the next round, the following method was made use of:—The gas from 6 was transferred to the empty reservoir A; and then, by lowering the reservoir of 6, mercury rose in the tube issuing from J, and expelled all the heavy gas in the connecting tubes into 6. The clip K was then closed, and by opening the stopcocks 1*a* and 6*a*, so that communication took place between jars 1 and 6, the small quantity of gas in 6 was transferred to 1. The apparatus was now ready for a second round.

The Fractional Diffusion of Air.

In order to test the working of the apparatus, a set of diffusions was carried out with air. After four rounds, comprising twenty-four diffusions, the light portion contained 17·37 per cent of oxygen and the heavy portion 22·03. A fairly rapid separation was thus being effected, considering the closeness of the densities of nitrogen and oxygen.

The Fractional Diffusion of Nitrogen.

A similar set of experiments was carried out with nitrogen, prepared by the action of solutions of ammonium chloride on sodium nitrite, in presence of copper sulphate. The gas was dried and passed over red-hot iron prepared by reduction of ferric oxide in order to remove any oxygen or to decompose any oxides of nitrogen which might be present. After thirty rounds, involving 180 operations, the "light" portion of the nitrogen, after purification by circulation over copper oxide, had not altered in density. It must therefore be concluded that nitrogen is homogeneous as regards the relative density of its individual molecules.

The Fractional Diffusion of Helium.

The first sample of helium employed was prepared from samarskite and cleveite. After seventeen rounds, involving 102 operations, the diffusion rates of the lighter and heavier portions were measured. The first gave a density, calculated from this rate, of 1·807, and the second of 2·128. The same gas was re-diffused until in all thirty rounds had been carried through, involving 180 operations. The light fraction now showed the density (measured diffusion rate against hydrogen) 1·816, and the heavy fraction 2·124. These gases were then circulated; the diffusion rate of the lighter portion pointed to a density of 1·811; the heavier gas was diffused into three portions, of which the more rapidly diffusing had a "diffusion density" of 1·906, and the less rapidly diffusing of 2·032. The lightest gas of all (diffusion density = 1·811) was weighed, and had a "real" density (O=16) of 2·021; the mixture of the heavy products gave the real density, 2·153. The refractivity of the heavy portion, measured against helium from cleveite, undiffused, yet purified from all removable gases, which had the density (weighed) 2·076, was 1·078, the refractivity of the undiffused gas being taken as unity.

A fresh quantity of helium was next prepared from cleveite, and the former diffused samples were stored in tube-reservoirs for future use. The new helium was washed with caustic soda, but not otherwise purified. This gas was now put through fifteen rounds, comprising 90 operations, and the light portion in jar 6 was purified by circulation over magnesium and copper oxide. Its refractivity was 0·9752 of that of the uncirculated helium. Its density by weighing was 1·979. Owing to the cracking of the glass apparatus the main bulk of the specimen was lost. It may be here interesting to chronicle that the remaining portion was inhaled through the nose and mouth; it possessed neither smell nor taste.

The contents of No. 5 were therefore purified and weighed; its density was 2·049.

The contents of No. 1 were also purified by circulation, and had a gravimetric density of 2·245. It lost on circulation a considerable amount of nitrogen which was estimated as ammonia by treatment of the magnesium containing nitride with water. As we are certain that there was no entry of air in preparing the gas, the 34 c.c of nitrogen must have been evolved from the mineral. It may have been occluded on the surface of the powdered mineral; it need not be remarked that before heating the mineral a nearly perfect vacuum was made in the tube, and that there was no leakage during the operations. We have previously found traces of nitrogen in gas prepared from cleveite; but not all specimens give off that gas. Supposing, however, to take the worst view, the nitrogen had been derived from leakage of air, it would correspond to only 0·3 c.c. of argon.

The contents of jar No. 2 were also purified and weighed. During the purification hardly a trace of nitrogen was removed. The density was 2·209. We have thus:—

Jar No. 1 contains gas of density	..	2·245
,, 2	,,	,,	..	2·209
,, 6	,,	,,	..	1·979

The light gas which had previously been stored in tubes was now mixed with the light gas from the second set of diffusions, and the mixture was re-diffused fifteen times, involving 90 operations. The density of the lightest portion of this helium was determined by weighing, and found to be 1·988. The helium had, therefore, not been made sensibly lighter by re-diffusion. The mean of the two determinations may be taken as the true density of pure helium; it is 1·98. The refractivity of this sample measured against hydrogen and multiplied by the ratio between hydrogen and air, viz., 0·4564, gives 0·1238. This specimen of light helium of density 1·988 was placed in one of the refractivity tubes, and the lightest helium of the former preparation (density = 1·979) in the other. They had the same refractivity (1000 to 1004). The contents of No. 1, obtained from the mixture of light gases, had the density 2·030, showing that only a little heavier material had been withdrawn.

The lighter fractions of helium were then sealed up in glass reservoirs and stored. The heavier portions were placed in the diffusion apparatus and submitted to methodical diffusion.

After fifteen rounds (ninety operations) the heaviest fraction had density 2·275, the lightest 2·08. The refractivity of the heaviest gas was next determined and

found to be 0·1327. This gas examined in a Plücker's tube showed brilliantly pure helium lines, but along with these the reds and green groups of argon. Calculating from the density of this gas it should contain 1·63 per cent of argon according to the equation $1·961x+20y=2·275$. Calculating from the refractivity the percentage of argon should be 1·05, from the equation $1·245x+0·9596y=13·33$. A mixture of 99 per cent of the purest helium, and 1 per cent of argon was made, and it showed the argon spectrum with about the same, or with somewhat less intensity than the heaviest gas. Finally, the heavy gas was diffused to the last dregs, so that only about 0·5 c.c. remained undiffused; and this small residue, transferred to a Plücker tube, showed the argon spectrum with only a trace of the spectrum of helium. The yellow line and the bright green line were visible, but feeble. This spectrum was compared with that of a mixture of argon with a trace of helium, and nearly the same appearance was to be seen. With the jar in parallel and a spark gap interposed the blue spectrum of argon was equally distinct in both tubes; and, more important still, *there was no trace of any unknown line.* It appears, therefore, that helium contains no unknown gas, nor is it possible to separate it by diffusion into any two kinds of gas; all that can be said is that most minerals which evolve helium on heating also evolve argon in small quantity. This accounts for the difference in density observed in different samples of helium; and in one instance, viz., malacone, the amount of argon evolved on heating the mineral, though small, was much in excess of the helium, so far as could be judged by the spectrum.

In the light of the experiments of which an account has here been given, it is necessary to re-consider the deduction drawn by Professors Runge and Paschen from the complex nature of the spectrum of helium as regards its complex nature. Sir Norman Lockyer has already pronounced in favour of the supposition that helium is a mixture, chiefly on the ground that in the spectra of certain stars some, but not all, of the helium lines are observable. It appears to us that this may well be accounted for by the hypothesis that the differences of temperature and pressure in the stars might produce variations in the spectrum of helium. If a jar and spark gap be interposed while observing the visible spectrum of helium, a profound alteration is to be noticed. The yellow line D_3 is to be seen near the electrodes, and is faint in the capillary portion of the tube, and one of the red lines disappears. The change is not as remarkable as in the case of argon, but is quite distinct and characteristic. Then, as before remarked, the green line becomes relatively stronger at low pressures, so that the light evolved in the tube is no longer the usual brilliant yellow, but dull greenish purple. Is it not likely that the conditions obtaining in the stars may account for the absence of some of the lines ordinarily visible?

If the hypothesis of Runge and Paschen is correct, then the two gases to which they attribute the complex spectrum of helium must have nearly the same density. It has already been shown that by means of the apparatus used for the fractional diffusion of gases it is possible to effect a fair separation of the constituents of air after a few rounds. If the supposed constituents of heliumdiffer in density in as high a proportion as 14 to 16, it is certain that some separation would have been effected. As there has been no such separation, the legitimate inference is that the density of the two supposed constituents does not differ by so great an amount, or that their existence is imaginary. It appears to us that too little is known regarding the nature of the vibrations which cause spectra to make it legitimate to theorise on the subject. It is surely conceivable that an atom may possess such a structure as to render it capable of propagating two different sets of vibrations, each complete in itself, and each resembling the other in general form. Yet it must be acknowledged that our experiments have not disproved the existence of two gases in helium of approximately the same density; in fact it may be contended that helium is a pair of elements like nickel and cobalt.

We are disappointed in the result of this long research, because we had thought it not improbable that an element of density 10 and atomic weight 20 might prove to be the cause of the fact that different samples of helium possess different densities, according to the mineral from which they are extracted, and also of the separation of helium into portions of different densities by diffusion. We still regard it as by no means improbable that further research will lead to the discovery of the "missing" element, and this appears to be a fitting opportunity of stating our reasons for the belief.

The difference between the atomic weights of helium and argon is $40-4=36$. Now, there are several cases of such a difference. If we compare the groups of which the first members are fluorine, oxygen, nitrogen, carbon, boron, beryllium, and lithium, we obtain the following table:—

	At. wt.			At. wt.	
Fluorine ..	19·0	16·5	Boron ..	11·0	16·0
Chlorine ..	35·5	19·5	Aluminium ..	27·0	17·1
Manganese ..	55·0		Scandium ..	44·1	
Oxygen ..	16·0	16·0	Beryllium ..	9·1	15·2
Sulphur ..	32·0	20·3	Magnesium ..	24·3	15·8
Chromium ..	52·3		Calcium ..	40·1	
Nitrogen ..	14·0	17·0	Lithium ..	7·0	16·0
Phosphorus ..	31·0	20·4	Sodium ..	23·0	16·1
Vanadium ..	51·4		Potassium ..	39·1	
Carbon ..	13·0	16·3	Helium ..	4·0	16·0
Silicon ..	28·3	19·8	? ..	20·0	20·0
Titanium ..	48·1		Argon ..	40·0	

The elements helium and argon have been given a provisional place.

The differences between the extreme members of these small groups are given in the short table which follows:—

Maganese—Fluorine	36·0	Chromium—Oxygen ..	36·3
Vanadium—Nitrogen	37·4	Titanium—Carbon ..	36·1
Scandium—Boron ..	33·1	Calcium—Beryllium ..	31·0
Potassium—Lithium	33·1	Argon—Helium	36·0

The difference between the atomic weights of argon and helium, it will be seen, is not far removed from those of the other pairs of elements. It appears, therefore, not improbable that there should be an element with atomic weight 20, resembling both argon and helium in its properties. Yet it is not so certain that the middle element should resemble argon and helium, for in the table given it is seen that there are several examples of elements with a middle place which do not resemble those at the extremes. The question is perhaps best left open.

It will be remembered that the gases evolved from a great many minerals and mineral waters have been examined, and that in many cases they have been found to contain helium and argon. In no instance up to the present has any sample of the gases evolved on heating in vacuum been found to show unknown spectrum lines. The amount of argon, as proved by the account which we have just given of our experiments, is very small, and in the case of the gas from cleveite, investigated by Langlet, it is probable that argon was almost completely absent, for it possessed the density 2. In malacone, on the contrary, argon is present in larger amount than helium, although neither gas is obtainable from it in large quantity. It appears to us not beyond the limit of probability that in some as yet uninvestigated mineral the middle member of the helium group may be discovered. When it is considered that germanium, an element which has been recognised only in one of the rarest of minerals, argyrodite, is the middle element of the trio, silicon, germanium, and tin, of which the first and last members are common, it is surely not unreasonable to hope that the middle member of the helium trio may ultimately be found. The amount of helium in fergusonite, one of the

minerals which yields it in fair quantity, is only 33 parts by weight in 100,000 of the mineral, and it is not improbable that some other mineral may contain the missing gas in still more minute proportion. If, however, it is accompanied in its still undiscovered sources by argon and helium, it will probably be a work of extreme difficulty to effect its separation from these gases.

Addendum.—Since this paper was written, Professors Runge and Paschen, in a communication to the British Association in August last, have withdrawn their contention that helium is a mixture, or, perhaps more correctly stated, they now ascribe to helium the same complexity as that of oxygen, the spectrum of which may also be arranged in two series, each consisting of three sets of lines. As oxygen has not yet proved to be complex, the surmise that helium is complex therefore falls to the ground.

FERGUSONITE, AN ENDOTHERMIC MINERAL.*

By WILLIAM RAMSAY Ph.D., LL.D., Sc.D., F.R.S.,
and
MORRIS W. TRAVERS, B.Sc.

THE mineral fergusonite, discovered by Hartwall, occurs in felspar and mica deposits, in the same manner as most of the rare Norwegian minerals, such as euxenite, orthite, samarskite, &c.. The position in which such minerals are found, embedded in masses of felspar, or encrusted with mica, leaves the question of their origin an open one. Whether they are deposited in the felspar by water, or whether they are contemporaneous with the felspar, is a matter of speculation. Fergusonite is a black lustrous mineral, not unlike obsidian in outward appearance, but of considerably higher density. Seen under the microscope, even with the highest power, there is absolutely no sign of crystalline structure, though in thin slices the substance is translucent, and transmits brown-yellow light. It is, however, macrocrystalline, occurring in quadratic sphenoids. It is quite homogeneous, and displays no sign of cavities. Like similar minerals, it contains helium, which is expelled on the application of heat.

But this mineral presents a peculiarity, which has led us to publish this note. When heated to a temperature not exceeding 500° or 600°, it suddenly becomes incandescent, and evolves much of its helium; while its density decreases.

The analysis of the mineral was kindly undertaken by Miss Emily Aston, to whom we desire to express our indebtedness. The mineral has been previously analysed by Hartwell, its discoverer, and by Weber, and, for the sake of comparison, we quote the earlier analyses (Rammelsberg's "Mineralchemie," p. 401):—

Composition of Fergusonite.

	Miss Aston.	Hartwell.	Weber.
Oxides of niobium and tantalum	40·95	47·75	48·84
Oxides of yttrium, erbium, &c..	31·09	41·91	38·61
Oxides of cerium, &c	13·87	4·68	3·05
Uranium dioxide .. .. .. 3·36	—	0·95	0·35
Uranium trioxide . .. .. 3·81	—	—	—
	7·17		
Titanium dioxide	4·56	—	—
ZrO_2	—	3·02	6·93
Silica	1·42	—	—
Ferric oxide	1·55	—	—
FeO	—	0·31	1·33
Lead oxide	0·16	—	—
SnO_2	—	1·00	0·35
Copper oxide	0·12	—	—
	100·89	99·62	99·46

* A Paper read before the Royal Society, January 20th, 1898.

The oxides of niobium and tantalum were converted into double fluorides of these metals with potassium fluoride; and on examination of the crystals under the microscope, they were seen to be almost entirely of one form. They were easily soluble in water, and, from previous experience with these compounds, we were able to recognise them as potassium-niobium oxy-fluoride. There appears to be hardly any tantalo-fluoride present in the possible mixture. The uranium dioxide was estimated by heating the mineral with dilute sulphuric acid in a sealed tube, and titrating the dioxide with potassium permanganate. The trioxide was calculated by difference from the total uranium. The cerium metals were separated, as usual, by means of a saturated solution of potassium sulphate.

It is thus seen that fergusonite is mainly a niobate of yttrium, containing oxides of uranium, but in no great quantity.

The gases evolved by the incandescence of nearly 5 grms. (4·852) of the mineral, heated in a vacuous tube, had the following composition:—

	Total gas. C.c.	Per grm. of mineral. C.c.	Per cent.
Helium	5·24	1·080	75·50
Hydrogen	0·38	0·078	5·47
Carbon dioxide ..	1·19	0·245	17·14
Nitrogen	0·13	0·027	1·88
	6·94	1·430	99·99

The remaining mineral was mixed with hydrogen-potassium sulphate, and heated to redness. More gas was evolved; oxygen, resulting from the decomposition of the sulphuric anhydride, was present in considerable quantity. The sulphur dioxide and the carbonic anhydride were removed by passing the gases through soda-lime, before it entered the pump; hence they do not appear in the analysis.

	Total gas. C.c.	Per grm. of mineral. C.c.	Per cent.
Helium	3·48	0·733	60·3
Nitrogen	0·42	0·088	7·3
Oxygen	1·87	0·394	32·4
	5·77	1·215	100·0

The mineral taken weighed 4·744 grms.

The density was determined before and after heating. Great care was taken to make sure of the absence of air-bells, by warming the powdered mineral under water in a vacuum before weighing it.

Density before heating	5·619
„ after „	5·375

It is thus seen that the mineral loses density on incandescence.

The amount of heat lost by this curious mineral in parting with its helium was determined. The plan of operation was to burn in oxygen a known weight of hydrogen, ascertained by measuring it, under a small platinum crucible, in a calorimeter. The rise of temperature was noted. This operation was repeated several times, so as to standardise the calorimeter. Some grms. of mineral were then placed in the crucible, and the operation was repeated; the heat evolved by the incandescing mineral added itself to that from the burning hydrogen, and the rise of temperature was greater. Knowing the heat of combustion of hydrogen, a simple calculation gave the heat evolved by the exothermic change in the mineral. The actual data are as follows:—

	I.	II.	III.	IV.
Rise of temperature per grm. of hydrogen ..	14·65°	14·68°	14·47°	14·56°
Additional rise for 6·0595 grms. mineral	2·13° = 0·352° per grm.			
Additional rise for 4·0830 grms. mineral	1·38° = 0·338° per grm.			
Mean rise per grm. hydrogen	14 59°			
Mean rise per grm. mineral	0·345°			
Heat of combustion of 1 grm. hydrogen	34200 calories.			
Heat of decomposition of 1 grm. mineral	809 calories.			

In these experiments a correction was, of course, introduced for the change of temperature of the calorimeter during the experiment, due to the temperature of the surrounding air being higher or lower than that of the calorimeter.

The percentage of helium in the mineral, by weight, is 0·0194, evolved on incandescence, and on further heating, 0·0132; the total percentage is 0·0326.

Dr. Shields was so kind as to determine the specific heat of fergusonite. A Bunsen's calorimeter, in thorough working order, was used. The data are:—

Weight of mineral	8·789 grms.
Temperature before introducing into calorimeter	17·3° C.
Deflection (1 m.m. = 0·001053 K) ..	154·4 m.m.
Mean specific heat between 0° and 17·3°	0·1069

Various questions are raised by the behaviour of this interesting mineral. Its evolution of heat, accompanying its parting with helium, suggests the idea that it is a true of endothermic compound of helium. Had its density, as is the case with alumina, and with other oxides which rise spontaneously in temperature when heated, increased instead of decreasing, the evolution of heat might justly have been ascribed to polymerisation. But an evolution of heat, accompanied by a *fall* in density, leads to the conjecture that the loss of energy is the result of the loss of helium; and that, conversely, the formation of the compound must have been concurrent with a gain of energy. That the helium is actually in combination, and not retained in pores in the mineral, is evinced by there being no pores in which the helium might be imprisoned. Surface-absorption is equally out of the question, for the mineral is compact. The only remaining possibility is that the helium is in chemical combination. And if this is true, then the compound must be an endothermic one.

The question next arises, with what constituent of the mineral is the helium in combination? This question cannot at present be answered. All that can be said is that the amount of helium does not appear to depend on the total percentage of uranium, although minerals containing uranium usually (probably always) contain this element. Even in English pitchblende there was found a trace of helium. And in malacone, a mineral containing no uranium, a trace of helium was found; also in a specimen of meteoric iron. The presence of niobic and tantalic anhydrides, and of the yttrium group of elements, is also favourable to its presence. But the proportion between the weight of the helium and that of the other elements present makes any calculation of the atomic relations between the helium and the other elements out of the question.

There is one other substance at least which decreases in density while it evolves heat; that substance is water, in changing into ice. The effect of compressing ice is to lower its melting-point, and at the same time to reduce its heat of fusion. At a sufficiently high pressure there would be a continuous transition from ice to water, no heat change taking place during the transition. Matters would be in a similar condition to those which accompany the change of a liquid into gas at the critical temperature; the smallest alteration of temperature would be enough to bring about the change. In speculating on the origin of such a remarkable compound, is it not allowable to guess that it represents a condition of our earth realised only before solidification had set in? That these minerals, containing the rare elements, represent a portion of the interior of our planet; and that, under the enormous pressure obtaining at the centre, combination with helium was an exothermic event; and that such compounds, having by some unexplained accident come to the surface of the globe, where they are no longer exposed to such pressure, they have, in consequence of the change, become endothermic? The frequency of the helium spectrum in the stars, and its presence in the sun, makes it less improbable that some such explanation may lie not far from the truth.

There are at least two other minerals, gadolinite and æschinite, which exhibit endothermic properties. But these minerals, instead of decreasing in density on ignition, increase. The following table shows the gases evolved when they are heated, their densities before and after heating, and the loss of weight which they suffer:—

	Gases evolved. C.c. per grm.				Density.		
	H_2.	CO.	CO_2.	He.	Before.	After.	Loss of weight.
Gadolinite	0·700	0·011	1·060	none	4·289	4·371	0·82
Æschinite	0·458	none	0·215	0·243	4·685	4·793	1·018

It is to be noticed that only the æschinite contains helium, and that in very small quantity.

The fact that these minerals increase in density, and that only one yields helium, places them in a different class from fergusonite. Moreover, the rise of temperature is not to be compared to that seen with fergusonite, for the glow is barely visible.

ON THE PREPARATION AND PROPERTIES OF PERCARBONATE OF POTASSIUM.

By A. VON HANSEN.

IN a memoir I recently published in collaboration with M. E. J. Constam (*Moniteur Scientifique*, August, 1897) we indicated the method of preparing percarbonate of potassium, as well as the general reactions of this new body. I have undertaken fresh researches, with the object of determining the conditions most favourable to its production, and to study some of its particular properties more closely.

As we have previously stated, percarbonate of potassium is obtained by the electrolysis of a concentrated solution of carbonate of potash maintained at a low temperature. The solution at the anode, clear at first, gradually assumes a milky appearance, because of the separation of a sky-blue solid body, viz., percarbonate of potassium. The product, however, is not free from ordinary carbonate. It is therefore indispensable to find conditions of temperature, concentration, and density of current, which will allow of the highest yield of percarbonate of potassium.

My first experiments were made with rather primitive apparatus, as previously described. A porous pot of 200 c.c. capacity was placed in a glass beaker of such capacity that the free space for the anode between the two receptacles was about 120 c.c. As anodes I made use of platinum spirals, and as cathodes sheets of nickel.

To follow the progress of the electrolysis, it was essential to have a method of titrating by which at any given moment the proportion of percarbonate present could be determined. The method we first adopted consisted of

pouring the solution of percarbonate into an excess of a solution of Mohr's salt, and to titrate the excess of unoxidised iron with permanganate of potash; but this was abandoned as giving doubtful results. I subsequently noticed that percarbonate of potassium treated with dilute sulphuric acid decomposes quantitatively into sulphate of potassium, carbonic acid, and peroxide of hydrogen. This latter can be easily titrated with permanganate of potash.

In all my experiments I have therefore thus determined the proportion of percarbonate of potassium in the anode solution at regular intervals of time. As for the density of the current, that was determined by Oettel's method.

a. *Influence of Temperature.*

If we commence the electrolysis at $-15°$ we notice that slight variations of temperature have no appreciable effect on the return, if the solution at the anode is very concentrated. The temperature has even been raised to 0° without the reaction being diminished. On the other hand, with solutions of carbonate of potassium of a density below 1·52, the useful return by the current diminishes as the temperature rises. It therefore follows that towards the end of the operation, when the concentration has been diminished by the separation of the percarbonate of potassium, the temperature ought to be lowered.

b. *Influence of Concentration.*

If the concentration of the liquid at the anode varies ever so little from saturation, we obtain but little, if any, percarbonate in the solid state, on account of the great solubility of this latter body in dilute solutions of carbonate of potassium. As the concentration diminishes, we notice a decrease in the useful effect of the current,—not so much because of the decomposition of the percarbonate already formed, as by reason of the formation of bicarbonate of potash. This latter is precipitated in large quantities in the crystalline state.

c. *Influence of the Density of the Current.*

To obtain a product rich in percarbonate of potassium it is essential that the density of the current should be very high. A current of low density favours the formation of bicarbonate of potassium. In a series of experiments, where the density of the current varied from 0·5 to 2 ampères per square decimetre, the proportion of percarbonate produced varied from 25 to 55 per cent. Each experiment was carried out on a solution of carbonate of potassium of 1·56 density, and the temperature was kept constantly at $-10°$. By increasing the density of the current to 30 and 60 ampères per square decimetre, the proportions of percarbonate of potassium produced, rose to 85 and 95 per cent. In all these experiments, then, it appears that—everything else being equal—a good return of percarbonate of potassium is correlative with a high current density, and a concentration as near saturation as possible. It is not absolutely necessary to maintain the temperature at $-12°$, if we only take care to keep the liquid at the anode as near saturation as possible.

The density of solutions of *pure* carbonate of potassium, saturated at the ordinary temperature, is from 1·555 to 1·565. It is curious to note that in lowering the temperature of these saturated solutions there is no separation of any solid salt, although such a separation takes place with ease if we use solutions of commercial carbonate of potassium, even when the temperature is lowered only a few degrees below zero.

To follow the progress of the reaction I took, at regular intervals, a known volume of the anode solution, and titrated the percarbonate of potassium. Although the liquid was carefully stirred before taking each sample, it is a matter of some difficulty to obtain a sample representing the average contents of the apparatus. To do the titration, 1 c.c. of the anode solution is poured into 150 c.c. of dilute sulphuric acid, and the peroxide of hydrogen formed is titrated with permanganate of potash. Among the numerous experiments I have made in this manner I will pick out a few, of which I now give the details.

I.

Density of the anode solution: 1·550.
Volume of the anode solution: 55 c.c.
Density of the current: 40 ampères per square decimetre.

Ampères.	Volts.	Temperature. °C.	Time in minutes.	Solution of $KMnO_4$. C.c.	Percarbonate. C.c.	Percarbonate per ampère-hour.
2·5	7·3 to 7·6	−11° to −10°	15	2·14	0·0375	3·1
2·5			30	4·74	0·0850	3·4
2·5			45	7·15	0·1199	3·3
2·5			60	9·18	0·1609	3·3
2·5			75	12·09	0·2103	3·4
2·5			90	13·30	0·2331	3·1

At the commencement of the operation the useful return from the current is thus fairly constant; but if we prolong the experiment it decreases rapidly, on account of the diminution of the concentration: this diminution is due to the formation of bicarbonate of potassium.

II.

Density of the anode solution: 1·560.
Volume of the anode solution: 150 c.c.

The anode was formed of a platinum wire 48 c.m. in length and 0·0345 c.m. diameter; the total surface was 5·2 square centimetres; current intensity = 3 ampères; difference of potential at the electrodes = 8·1 volts.

We obtained 19·5 grms. of the salt, containing 92 per cent of pure percarbonate of potassium. Duration of the experiment, two hours and thirty minutes. Total quantity of electricity, 7·5 ampère-hours. Return of percarbonate per ampère-hour, 2·4 grms.

At the termination of the experiment titration showed 21·84 grms. of percarbonate in the total volume of the solution, or 2·9 grms. per ampère-hour. The filtered liquid was also titrated; it contained 3·74 grms. of percarbonate of potassium.

At the end of the operation the density of the anode solution was 1·42. During the entire time of the experiment the temperature varied from $-12°$ to $-10°$. As a rule, at the beginning of the electrolysis, we can detect the characteristic odour of ozone, but this gradually disappears as the operation proceeds.

As cathode solution we use a less concentrated solution of carbonate of potassium, so as to prevent the salt crystallising out. As anode, the only convenient metal is platinum. Iron, nickel, and copper are all attacked very rapidly. An aluminium vessel serves very well to hold the refrigerating materials. With 8 kilogrms. of a mixture of ice and sea-salt we can keep the temperature at $-15°$ for three hours.

The process I have just described is not very practicable when we want to produce large quantities of percarbonate of potassium, both because of the diminution of the concentration which goes on and the lowering of the useful effect of the current which is the natural consequence.

For preparing the percarbonate on the large scale we make use of an apparatus provided with an appliance by means of which we can introduce fresh portions of potassic carbonate solution into the lower part of the positive compartment, as the percarbonate is precipitated. As the density of the fresh solution is greater than that of the electrolysed solution, the latter will be displaced mechanically, and will run off through an orifice provided in the upper part of the jar. By taking certain precautions we can maintain the operation continuously for a considerable number of hours.

The precipitated percarbonate is filtered on a filter-pump; it contains 87 to 93 per cent of pure percarbonate of potassium. It is then spread out on porous plates,

and placed in an apparatus traversed by a current of dry air: by this means it can be dried very rapidly, and the resulting salt does not contain more than 2 to 4·3 per cent of water. By first drying the air over concentrated sulphuric acid and melted chloride of lime, and prolonging its action for twelve hours, we can further reduce the proportion of moisture present to 0·6 or 0·8 per cent. Towards the end of the drying the temperature of the air may be raised to 40°. Above this temperature decomposition commences. By heating the air to 100° the proportion of percarbonate present drops by 6 per cent at the end of an hour, and by 10 per cent after two hours.

Percarbonate of potassium thus obtained is an amorphous powder of a slightly blue tint. The blue colouration of the wet salt almost completely disappears on drying.

Percarbonate of potassium decomposes easily, giving up its oxygen to oxidisable bodies. Its instability, however, is not so great as would have been at first thought; to decompose it rapidly it is necessary to submit it to a temperature of 200° to 300°. Immersed in water it only decomposes slowly. If, for example, we place 0·3 grm. of percarbonate of potassium into 50 c.c. of water, and then titrate with permanganate of potash, after adding dilute sulphuric acid, after the lapse of half an hour, we find that the loss is hardly 1 per cent. But at a higher temperature the splitting up into oxygen and bicarbonate of potassium takes place very rapidly. Thus percarbonate of potassium constitutes a primary body most convenient for the preparation of oxygen in laboratories. After having put the salt in water, it is only necessary to raise the temperature to 45° to obtain a very regular flow of gas. The decomposition is complete without having to raise the temperature any higher than 45°, and we finally obtain a solution not containing any percarbonate at all. From 100 grms. of the salt we can obtain about 5 litres of oxygen. The traces of carbonic acid which might be given off at the same time are absorbed by an alkaline solution.

We have seen that, under the influence of dilute acid, percarbonate of potassium decomposes with the formation of peroxide of hydrogen; here is at once a simple method for rapidly preparing solutions of peroxide of hydrogen, and this is the more important as commercial peroxide of hydrogen changes very rapidly, whereas percarbonate of potassium keeps very well indeed if it has been carefully dried. It suffices to keep it in hermetically sealed glass flasks.

The percarbonate is but very slightly soluble in alcohol, and it has up to the present time been quite impossible to obtain it in crystals from its aqueous solution. If we saturate water at 0° with percarbonate of potassium, and then lower the temperature to −15°, we obtain a voluminous crop of crystals, but they are formed almost entirely of ice.

It is possible to enrich impure percarbonate of potassium by a very simple process. Into a moderately concentrated solution of caustic potash we place an excess of the percarbonate to be purified, and leave it for several hours at a temperature of −8° or −10°. Under these conditions the bicarbonate held by the percarbonate, is decomposed by the caustic potash with the formation of a neutral carbonate which goes into solution. By filtration we obtain a percarbonate containing a very small qnantity of caustic potash, which can be extracted by treating it with absolute alcohol. The final product then contains about 95 to 99 per cent of percarbonate of potassium.

I applied this system of purification to a percarbonate which titrated 78 per cent. Analysis gave me the following results:—

Substance used	0·5012 grm.
Carbonate of potassium ..	0·3912 ,,
Carbonic acid	0·1241 ,,
Water	0·0025 ,,
Oxygen	0·0434 ,,

The salt was placed in a porcelain boat in a tube of Bohemian glass, and the whole was warmed. The carbonic acid and the water were estimated in the ordinary way; the residue of carbonate of potassium was weighed with great care. The figures worked out into percentage give for the composition of the purified salt:—

Percarbonate of potassium..	95·68 per cent
Bicarbonate of potassium ..	3·84 ,,
Carbonate of potassium ..	0·35 ,,
Moisture	0·10 ,,
	99·97 ,,

I have not yet been able to isolate the percarbonates of sodium or ammonium. But I am carrying on a new research in that direction.—*Zeitschrift fur Electrochemie*, 1897, p. 455.

ON THE SEPARATION AND ESTIMATION OF IODINE, BROMINE, AND CHLORINE.

By AD. CARNOT.

Many methods have been proposed for the estimation of these three bodies in a mixture of haloid salts. In deciding to offer still another one, it is because it appears to unite the qualities of simplicity, rapidity, and exactness, which are not found altogether in any of the other already known methods.

I have made use of the excellent instructions given by Fresenius (Fresenius, *Chim. Quantit.*, sixth French edition, p. 406) for the estimation of the iodine, and I have profited by some observations of M. Dechan (*Chemie Soc.*, vol. xlix., p. 682; *Bull. Soc. Chim.*, vol. ii., p. 331, 1887), and of M. Baubigny (*Comptes Rendus*, vol. cxxv., November 2, 1897, p. 654) relative to bromine.

The new method is founded on the following reactions:—In a mixture of chlorides, bromides, and iodides in solution, sulphuric acid charged with nitrous vapours is able to entirely displace the iodine in the cold without acting on the hydrochloric or hydrobromic acids in any way; the iodine can then be entirely dissolved and removed by sulphide of carbon. By adding sulphuric and chromic acids the bromine can only be partially removed in the cold, but by heating to about 100° for about half an hour or an hour, and then letting it cool, and dissolving in sulphide of carbon, it can be entirely removed. In neither case is there a trace of chlorine set at liberty, the estimation of this body can then be made with nitrate of silver.

As for the iodine, it is estimated volumetrically by adding hyposulphite of sodium to the sulphide of carbon until the decolouration is complete; for the bromine we operate in the same manner, but first add a little iodide of potassium, then adding titrated hyposulphite of sodium until the violet colouration, caused by the free iodine exactly disappears.

A series of experiments made on most varying proportions of chlorides, bromides, and iodides, have proved the accuracy of the results, provided that the precautions about to be mentioned were duly observed.

I. *Iodine.*—The neutral solution of the salts, diluted to about 200 c.c. in volume, is introduced into a bulb-shaped funnel of 350 c.c. to 400 c.c. capacity, well closed at the top with a ground stopper, and at the lower part by a glass tap, made sufficiently strong as not to run any risk of breaking when heated in the water bath.

Into the cold solution we drop about ten drops of sulphuric acid saturated with nitrous fumes (produced by the action of concentrated nitric acid on starch), we then pour in from 10 to 15 c.c. of pure sulphide of carbon. The glass stopper is then fixed firmly in, and the whole shaken vigourously several times; the sulphide of carbon is now allowed to collect, shaking gently to help the small drops

Proportions taken for the experiment.						Hyposulphite used for		Weighed.	Found.		
Iodide. M.grms.	Bromide. M.grms.	Chloride. M grms.	I. M.grms.	Br. M.grms.	Cl. M grms.	I. C.c.	Br. C.c.	AgCl. M.grms.	I. M.grms.	Br. M.grms.	Cl. M.grms.
200	100	200	153·0	67·2	95·2	22·3	15·2	380	152·5	65·3	94·0
100	100	100	76·5	67·2	47·6	11·2	15·4	—	76·6	66·2	—
100	200	100	76·5	134·4	47·6	11·2	31·0	192	76·6	133·3	47·5
20	40	200	15·3	26·9	95·2	2·2	6·3	—	15·0	27 1	—
5	50	200	3·8	33·6	95·2	0·6	7·8	—	4·1	33·5	—
1	100	600	0·8	67·2	285·6	0·1	15·3	—	0·7	65·8	—
—	20	500	—	13·4	238·0	—	3·1	—	—	13·3	—
—	10	200	—	6·7	95·2	—	1·5	—	—	6·4	—
—	5	200	—	3·4	95·2	—	0·7	—	—	3·0	—
—	1	200	—	0·7	95·2	—	0·1	—	—	0·4	—
100	100	20	76·5	67·2	9·5	11·2	15·5	39	76·6	66 6	9·6
100	100	5	76·5	67·2	2·4	11·2	15·6	10	76·6	67·1	2·5

which adhere to the sides of the glass to become detached and sink to the bottom. The sulphide of carbon is of a deep violet colour if much iodine is present, and pale violet, or even rose colour, if there is only a little; it is easily distinguished in the aqueous solution, and it fills the lower part of the bulb and the fine tube down to the tap. The tap is now carefully opened, and the coloured sulphide of carbon run on to a filter-paper moistened with water; the tap is shut the moment the aqueous solution reaches it. Another 10 c.c. of sulphide of carbon is added, and the shaking repeated as before; the reagent is, as a rule, but very faintly coloured with iodine the second time; three or four more drops of nitrous sulphuric acid are then added, and after a further agitation, which ought not to produce any change of colour if the first operation was properly carried out, the sulphide of carbon is allowed to collect, and run off into the same funnel, which must be covered over by a sheet of glass to prevent evaporation.

The introduction of two or three c.c. of sulphide of carbon, and one or two drops of nitrous sulphuric acid, enables us to collect the small drops of sulphide which may remain on the surface of the liquid, to make sure that the displacement of the iodine is complete, and to wash out the small quantity of faintly coloured sulphide contained in the passage through the glass plug of the tap.

The sulphide of carbon, collected on a moistened filter, is well washed with cold water. Only the first washings are retained, and added to the aqueous solution in the bulb for the continuation of the analysis. By piercing the filter we can run the sulphide of carbon into a small glass-stoppered flask containing about 30 c.c. of a $\frac{1}{2}$ per cent solution of bicarbonate of sodium. Then by means of a small graduated burette we run in a titrated (decinormal or centinormal) solution of hyposulphite of sodium, until the sulphide of carbon is completely decolourised. The flask must be well shaken after each addition of the reducing agent; the reaction is most distinct, and the exactness of the results is as close as possible, not only in the presence of chlorides, as was observed by Fresenius, but also in the presence of bromides.

II. *Bromine.*—To estimate the bromine we pour a few cubic centimetres of 10 per cent chromic acid and three or four cubic centimetres of sulphuric acid, containing its own volume of water, into the large bulb; we then replace the glass stopper, taking care to fix it in very firmly. The bulb is then floated in a water bath at 100° for from half an hour to an hour; it is then taken out and allowed to become completely cold; sulphide of carbon is then introduced, and the operation proceeded with, as I have already explained for iodine, by three successive exhaustions. The sulphide of carbon is collected on a moistened filter, then washed with cold water until it is no longer acid. It is then run into a glass-stoppered bottle, where a little solution of iodide of potassium, and 30 cubic centimetres of bicarbonate of sodium is added to it. The bottle must be well shaken several times. The bromine displaces an equivalent proportion of iodide which, being set free, gives the solvent a violet colour which is much more easily visible than was the yellow tint produced by the bromine. The estimation of the iodine is made, as before, by titrated hyposulphite of sodium, and we have then only to multiply the weight of the iodine by the coefficient $\frac{80}{127}$ to get the weight of the bromine present.

III. *Chlorine.*—The acid solution from which the iodine and the bromine have been removed, and to which both the first washings have been added, is poured into a large beaker and diluted to about 500 c.c. Nitrate of silver is then added, and the whole heated to collect the chloride. The precipitate will be found to be slightly coloured by chromate of silver; to purify it the liquor is decanted after cooling, and replaced by a little warm water slightly acidulated with nitric acid; it is again allowed to cool, and the precipitate is then washed by decantation. The chloride of silver, now perfectly white, is dried and weighed on a tared filter with the usual precautions.

Of the three, the estimation of the chlorine is the one to which, as a rule, we attach the least importance. Instead of operating in the manner I have just described, we might nearly always be satisfied to estimate by difference; a volumetric method enables us to do this rapidly in the following manner.

We can operate on the solution deprived of iodine by dividing it into two portions. One is treated for the estimation of bromine only, as has been described; the other is precipitated by a measured quantity of titrated nitrate of silver. The excess of silver is then determined by means of titrated sulphocyanide, using iron-alum as an indicator. According to the estimation of the bromine, we know the quantity of nitrate of silver it has used, and, by difference, we can easily calculate the chlorine. Thus we need (and, above all, if the chlorides are present in much greater proportion than the iodides and bromides) only take one-tenth or one-fiftieth of the first neutral solution, add to it chromate of potassium as an indicator, and by means of a burette drop in titrated nitrate of silver until the appearance of the red colour of the chromate. Thus, taking from the nitrate of silver used the quantity which corresponds to the iodine and the bromine, we get what was precipitated by the chlorine.

The chlorine, it is seen, can be easily estimated by either of these methods.

The accompanying table, showing the results of a series of experiments made on both large and small proportions of each of these three bodies, enables us to appreciate the exactness which can be habitually attained by this method.

For a simple *qualitative research* for small quantities of iodine and bromine in the presence of a large excess of alkaline chlorides, the following plan is to be recommended:—

1. Separate the iodine in a small quantity of the neutral solution by means of nitrous sulphuric acid, and collect it in a few drops of sulphide of carbon. The violet or rose colouration is extremely sensitive.

2. The iodine having been eliminated, add to the solution, in a small flask, a small quantity of chromic and sulphuric acid, heat to boiling, and place over the opening a strip of yellow fluoresceine paper, described by M. Baubigny, both with regard to preparation and sensitiveness to bromine. The faintest traces of bromine will be shown by the characteristic rose colour. — *Comptes Rendus*, cxxvi., No. 3.

THE REVIVAL OF ALCHEMY IN FRANCE.*

By H. CARRINGTON BOLTON, Ph.D.

Recent discoveries in physics, chemistry, and psychology have given disciples of Hermes renewed hopes, and the present position of chemical philosophy has given the fundamental doctrine of alchemy a substantial impetus; the favourite theory of a *prima materia*, or primary matter, the basis of all the elementary bodies, has received new support by the discoveries of allotropism of the elements, isomerism of organic compounds, the revelations of the spectroscope, the practical demonstrations by Norman Lockyer, the experiments on the specific heat of gaseous bodies at a high temperature by Mallard and Le Châtelier, the discoveries of Sir William Crookes, as set forth in his monograph on "Meta-elements," the discovery by Carey Lea of several singular allotropic forms of silver, and, most weighty of all, the mass of related facts and phenomena which find their ultimate expression in the Periodic Law of the Elements, so that many chemists of the present day are inclined to believe in the mutual convertibility of elements having similar chemical properties. Daniel Berthelot, in his notable work entitled "De L'Allotropie des Corps Simples," boldly affirms his belief in the unity of matter. He says: "Without seeking to find in any one of the known elements the generator of the others, can we not invoke the facts that we have revealed in our study of carbon in favour of the hypothesis of a unique matter unequally condensed?" And elsewhere he writes: "The transmutation of an element is nothing more than the transformation of the motions which determine the existence of said element, and which gives it special properties into the specific motions peculiar to the existence of another element."

Simultaneously with the development of the truly scientific aspect of alchemical theory, there has arisen an extraordinary revival of the metaphysical side of the question; this goes hand in hand with the interest in chiromancy, astrology, theosophy, and occult sciences which occupy so large a place in modern thought, literature, and polite society on both sides of the Atlantic. This tendency to cultivate the esoteric manifests itself in the study of the Kabala, the investigation of the mysteries of Buddhism, Confucianism, and other oriental philosophies, in researches into the phenomena of spiritualism so-called, and in the foundation of societies to study Psychic Force and the tenets of the followers of Madame Blavatsky; crystal-gazing, reading in magic mirrors, slate-writing, planchette, the quasi-scientific study of apparitions, of table-turnings, of rappings by unseen powers, of telepathy, of subliminal self, are now regarded as legitimate pursuits in no wise necessarily associated with the black arts of mediæval times, provided only they are conducted in a spirit of enquiry, and for the purpose of discovering the latent power underlying these phenomena. And this line of research receives stimulus from the results secured by students of experimental psychology, of hypnotism, from such discoveries as the phenomena of the X-rays, and from the transcendental physicists who theorise on the miraculous consequences of four dimensional matter. Crowded lecture halls reward exhibitions of trance mediums, speakers on theosophy, palmistry, and occultism; in lower walks of life fortune-tellers and clairvoyants reap a modest harvest; books treating of occult themes enjoy great notoriety; writers of fiction find it profitable to introduce the mysterious into the children of their brains; even secular journals, especially those of France, give space to the all-absorbing discussions on hermetism; these are some of the evidences of great popular interest in the unknowable. Only persons with special intellectual equipment are able to measure, weigh, sift, and co-ordinate the novel phenomena gathered by researches in the field of hypnotism, psychology, and occultism; those of weaker mental powers fail to perceive the real significance of the discoveries, and are led away into unprofitable and dangerous superstitions.

In the Middle Ages alchemy was nurtured by ignorant superstition; now it is fostered by the prevalent devotion to esoteric studies; formerly the popular belief was in part supported by the fraudulent claims of impostors; now a higher standard of intelligence rejects the transparent tricks of imitators of Cagliostro. It is not by sleight-of-hand that the revival of alchemy is now being engineered, but by a company of educated charlatans.

The movement to resuscitate alchemical doctrines and practices has been particularly successful in France, where there are to-day four societies and a "university" claiming to possess occult knowledge of hermetic mysteries. These secret societies are named, "Ordre de la Rose-Croix," "L'Ordre Martiniste," "La Société d'Homéopathie Hermétique," and "L'Association Alchimique de France."

The first two of these societies seem to work on lines similar to Free Masonry, and claim that their secret mysteries were bequeathed by the last sages of Atlantis, and by the Lemures to their brethren in Asia and Egypt, dwellers in sanctuaries whence issued Krishna, Zoroaster, Hermes, Moses, Pythagoras, and Plato. The priestly Magi who preserved this lore in the temples of Thebes, Heracleopolis, Aphrodite, Pthah, and Serapis, were succeeded by secret alchemical societies of the first centuries of our era; then followed the Hermetic lodges of the Arabs, and these gave rise to the Templars, the Rosicrucians, and the Martinists.

The third society cultivates especially occult therapeutics, a system of medicine invented in the sixties by Count Cæsar Mattei, of Bologna, which unites the principles of Hahnemann with those of the Iatro-chemists, disciples of Paracelsus. This new departure in medicine publishes four monthly organs, and special treatises all its own.

The Alchemical Association of France is successor to the Société Hermétique, which was founded by the late Albert Poisson (†1894), also known by the pen-name "Philophotes." Its seat is in Paris. The objects of the Association, as set forth in its constitution, are "the theoretical and experimental study of evolution, and of the transmutation of bodies. Its members, with this end in view, study the processes of the ancient alchemists, and compare them with the work of modern chemists." These objects are to be accomplished as follows: "The Association proposes to assist in reviving the unitary doctrines of chemistry: 1st, by grouping the efforts of isolated workers by means of *L'Hyperchimie*; 2nd, by furnishing them the aid of advanced students; 3rd, by supplying, so far as possible, books and apparatus to its members. Researches of the members, when approved by the masters, should be forwarded in duplicate to the secretary-general; one will be printed in *L'Hyperchimie*, and the other will be preserved in the archives of the Association for the benefit of members who can secure it on demand." "Candidates for admission must pass an examination in: 1st, the theory and history of alchemy; and 2nd, the elements of physics and of chemistry (without mathematics). A diploma from a normal, polytechnic, or industrial school will be accepted in place of No. 2."

The affairs of the Association are controlled by the secretary-general, F. Jollivet-Castelot (of Douai), assisted

* Abstract of a Paper read to New York Section of the American Chemical Society, October 1, 1897. From *Science*, N.S., vol. vi., No. 154.

by seven councillors, who hold an annual meeting. There are at present (July, 1897) two honorary members, Camille Flammarion, the popular writer on astronomy, and August Strindberg, a Swede residing in Austria, author of several hermetic essays.* There are two other classes of members, masters (*maîtres*), who are chosen from the ordinary members by the Council after an examination of their writings, and ordinary members (*membres adhérents*), of which the number is unlimited. Modest dues entitle the members to the organ of the Association, *L'Hyperchimie*, a monthly review of alchemy and hermetism founded in 1896.

The councillors of the Alchemical Association have combined with the active members of the other societies named to establish a Université Libre des Hautes Etudes. At present this includes three faculties:—

I. Faculté des Sciences Hermétiques, of which the Association Alchimique forms a section. The director of this faculty is Dr. G. Encausse, and the course of instruction embraces the study of the *Tarot*, alchemical philosophy and practice, occultism, mysticism, Hebrew, &c.; the curriculum leading to the "baccalauréat-en-Kabbale" is under the supervision of the group of esoteric students, while candidates for the degrees of master and doctor are under the direction of the Martinist Order.

II. Faculté des Sciences Magnétiques, represented by the Ecole de Magnétisme de Paris, and under the direction of M. Durville; it has branches at Lyons, Bordeaux, and other cities.

III. Faculté Spirite, comprising several sections of spiritism.

Each faculty preserves complete independence, being "united only by moral bonds destined to hasten expansion of the rational spiritualistic movement."

The nature of the instruction given at this University will appear in the review of the philosophy of its promoters.

One of the oldest workers in the Alchemical Association is the "Master" Théodore Tiffereau. In 1854-55 he sent to the French Academy of Sciences six memoirs in which he claimed to have discovered a method of converting silver into gold. Tiffereau had made his experiments in Mexico at great expense, supporting himself meanwhile by taking daguerreotypes. His process was repeated at the Mint, in Paris, before the assayer, M. Levol, but with little success. The substance of his memoirs was published in 1855 in a volume, entitled "Les Métaux sont des Corps Composés." Of this a new edition was published by Lermina in 1889. Tiffereau has never abandoned his claim, and as recently as October, 1896, he addressed another memoir to the Academy, in which he attempts to prove that the metal aluminum is a compound. Briefly stated his process is as follows: He placed in a stout glass tube a piece of aluminum foil with pure nitric acid, and sealed the tube hermetically. He then exposed the tube and contents to the sun's rays during two months; at the end of this time he opened the tube; it gave out an odour which he thought was due to ether, and it yielded a few grms. of crystals which he thought tasted like acetic acid. Since both ether and acetic acid are compounds of carbon, Tiffereau concluded that this element was derived from the aluminum. Analytical chemists would criticise this experiment in several points; they would say Tiffereau did not demonstrate the absence of carbon in the metal used, and that he depended upon smell and taste for proofs of the carbon compounds; the tongue and the nose are incontestably useful adjuncts to the reagents of a chemical laboratory, but additional tests for ether and acetic acid would have been more conclusive. In Tiffereau's recent writings he attributes the transmutation of a base metal into the most precious one, to the action of the "microbe of gold."

(To be continued).

* Dr. Stephen H. Emmens, of New York, has been added to the list of honorary members since writing the above.

NOTICES OF BOOKS.

The Early History of Chlorine. Alembic Club Reprints, No. 13. Edinburgh: Wm. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co., Lim. 1897. Pp. 48.

No. 13 of these interesting reprints consists of papers by Scheele (1774), Berthollet (1785), Guyton de Morveau (1787), and Gay-Lussac and Thenard (1809), and we are informed in the preface that the volume containing Davy's researches (No. 9) may be taken as a continuation of the present one.

The first paper, by Scheele, contains the account of his accidental discovery of chlorine: he noticed that when pure *spiritus salis* was poured on to finely-ground manganese, and let stand an hour in the cold, the solution became brown, and on warming gave off an odour like warm *aqua regia*; after a quarter of an hour both colour and smell had gone. He then goes on to describe the action of *marine* acid on manganese, and the phenomenon which occurs proves, he thinks, the presence of phlogiston.

In the next paper, by Berthollet, on "Dephlogisticated Marine Acid," the author still adheres to the idea of phlogiston, and he elaborates a new but erroneous theory that chlorine is the higher oxide of an unknown radical. By the time we get to Gay-Lussac and Thénard, ideas have changed, phlogiston is abandoned, and it is sometimes claimed that it was these authors who first established the elementary character of chlorine. It is of the greatest interest to notice the manner in which there early chemists were, so to speak, groping about in the dark, and with what untiring patience they laid the foundations for our modern accepted theories; who knows but that in another hundred years, or even less, we ourselves may not be proved to be as mistaken in many of our present theories as we think they were.

Researches on Molecular Asymmetry. By LOUIS PASTEUR (1860). *Alembic Club Reprints*, No. 14. Edinburgh: Wm. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co., Lim. 1897. Pp. 46.

THE two lectures which comprise this volume were published by the Chemical Society of Paris in 1861.

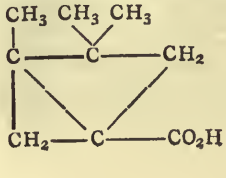
The author begins by reviewing the optical work done by Malus, Huygens, Newton, Arago, and Biot, especially on polarised light; he then goes on to discuss hemihedry in quartz, and then in crystals of organic substances. His own work on this subject, which forms the greater part of the book, is, however, so well known, that we need not go fully into it here; his remarkable discovery of the right- and left-handed tartrates, and the work he did on them, holds as good now as it did when first printed thirty-seven years ago, the whole forming a most interesting volume.

CORRESPONDENCE.

CAMPHOR AND ITS DERIVATIVES.

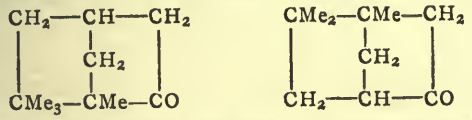
To the Editor of the Chemical News.

SIR,—In the recent discussion of camphor and its derivatives in the CHEMICAL NEWS two or three formulæ are proposed which appear to me inconsistent with established facts. Professor Perkin (CHEMICAL NEWS,, vol. lxxvi., p. 287) gives the following formula for isolauronolic acid—



This formula can scarcely be reconciled with the fact that the acid conducts itself as an unsaturated acid, reducing instantly an ice-cold neutral solution of potassium permanganate. It has also been shown (*Ber. d. Chem. Ges.*, xxix., 2327) that the acid readily takes up two atoms of hydrogen, on treatment with amyl alcohol and sodium. The resulting saturated cyclic acid gives an α-brom-derivative, and this, in turn gives the original isolauronolic acid when warmed with alcoholic potash. (In that paper the acid is called cis-campholytic acid, for reasons given in the *Am. Chem. Journ.*, xvii., 430). A reasonable explanation of these relations on the basis of Professor Perkin's formula appears to be impossible.

In the CHEMICAL NEWS (vol. lxxvi., p. 297) Dr. Forster discusses the following formulæ for camphor :—



He prefers the second formula. Of the two, however, the following considerations appear to prove that only the first could be true. The iso-nitroso-camphor of Claisen and Manasse gives α-camphoraminic acid on treatment with hydrochloric acid (*Ann. Chem.*, Liebig, cclxxiv., 80); this in turn gives aminolauronic acid by Hofmann's reaction (*Am. Chem. Journ.*, xvi., 506). β-Camphoraminic acid gives, by the same treatment, dihydroaminocampholytic acid. The relative rates of esterification of aminolauronic and dihydroaminocampholytic acids proves that, if only one of these acids contains a tertiary carboxyl-group, that group must belong to the aminolauronic acid (*Am. Chem. Journ.*, xviii., 686). But since, from the relation of that acid to isonitroso-camphor, its carboxyl must correspond to the carboxyl group of camphor, it follows that in the latter the carboxyl group is combined with a carbon atom of the nucleus, which is not combined directly with hydrogen.—I am, &c.,

W. A. NOYES.

Rose Polytechnic Institute,
Terre Haute, Indiana, January 8, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 3, January 17, 1898.

M. Schiaparelli, correspondent of the Astronomical Section, writes to deny the announcement of his death.

The Separation and Estimation of Iodine, Bromine, and Chlorine.—Ad. Carnot.—(See p. 67).

On the Mixture of Gases.—A. Leduc.—The author proposes as a new law for the mixture of gases—"The volume occupied by a gaseous mixture is equal to the sum of the volumes which would be occupied by the gases which form it at the pressure and temperature of the mixture." And, further, he affirms that, "in a mixture, each gas should be considered as being subject to the total pressure." In applying this rule to finding the density of argon, he found it to be 19·80, instead of 19·94 as found by Lord Rayleigh and Prof. Ramsay.

Determination of the Density of Gases on very Small Volumes.—Th. Schlœsing, jun.—This paper cannot be followed without the accompanying diagram. The author found, however, that his results were of much greater accuracy than he expected.

Spectrum of Cadmium in Vacuo.—Maurice Hamy.—The cadmium lamp, already described, gives at least twenty lines when the tube is heated to about 295° *in vacuo*. Some produce interference lines; of these, λ 644 is one. Its wave-length has been determined with great care by M. Michelson's method. Other lines have also been carefully measured, and are here given in a table.

Electrical Resistance of Crystallised Silicon.—Fernand le Roy.—Sticks of agglomerated silicon can easily be prepared of 40 sq. m.m. sectional area and 10 c.m. in length, having a total resistance of from 25 to 200 ohms, according to the variation in pulverisation, compression, and baking. The resistance of silicon, like that of carbon, decreases on heating. At a temperature of 800° the resistance diminishes 40 per cent.

Some New Compounds of the Cerite Metals.—M. André Job.—Will be inserted in full.

Aldehydate of Ammonia.—M. de Forcrand.—The interesting discovery by M. Delépine last month on the constitution of aldehydate of ammonium, has prompted the author to make known some results he obtained ten years ago. Pure and recently prepared aldehyd gave, when dissolved in water, +4·41 cals. at about +12°. Its neutralisation by NH_3 (17 grms. in 2 litres) gave +3·59 cals. after one minute; after that the temperature continues to rise for fifteen minutes, when he again found +3·60 cals., making a total of +7·19 cals. In a further series of experiments, perfectly pure solid aldehydate of ammonia, C_2H_7NO, gave as heat of solution +0·1 cal. for one molecule dissolved in 4 litres of water at +12°.

Oxidation of Ammoniacal Compounds by Ferments in the Soil.—E. Demoussy.—The study of nitrification in arable soils leads one to admit that the humus passes to the state of ammonia before being able to become nitrified, and that it is the resistance that it offers to the agents of decomposition that is the cause of the slowness of the formation of nitrates in soils. In some experiments made with methylamine in the presence of ferments in arable soil, nitrites appeared after the sixth day; being replaced by nitrates after a fortnight. The author concludes that, under the influence of the ferments in the soil, the amines are simplified, and by oxidation form ammonia, which only is able to pass directly to the state of nitrous or nitric acid.

Preparation of Gentianose.—E. Bourquelot and L. Nardin.—The authors have prepared gentianose from the fresh roots, in crystalline plates containing no water of crystallisation. It gives colourless aqueous solutions, and burns without leaving any residue; it melts at 207—209°; it is dextro-rotatory to polarised light, $\alpha_D = +31° 25'$ in aqueous solution.

Journal de Pharmacie et de Chimie,
Series 6, vol. vi., No. 12.

Colour of Amorphous Mercuric Iodide.—Maurice François.—Already inserted in full.

Basic Ortho-antimoniates of Potassium.—A. Delacroix.—A solution of 1 part of Sb_2O_5,K_2O and 2 parts of KHO was evaporated down on a water-bath at 100° *in vacuo*, and crystals were formed. These were separated from the alkaline mother-liquor and dried *in vacuo* on a porous plate. The Sb_2O_5 was estimated in the crystalline powder thus obtained by precipitating as sulphide; after moistening with a little HCl the potash was estimated by Rose's method; the water and a little CO_2 were estimated by difference. The results found were:—$K_2O = 25·30$ per cent, $Sb_2O_5 = 58·44$ per cent, $H_2O + CO_2 = 16·26$ per cent, which gives for the anhydrous salt free from CO_2 the formula $Sb_2O_5(K_2O)_{1·47}$. This leads the author to think that the neutral meta-antimoniate does not exist. The ortho-salt, when recently precipitated and prepared in the cold, loses one-third of its potassium when treated with CO_2, and gives a neutral ortho-antimoniate, $Sb_2O_5(K_2O)\frac{2}{3}$.

Impurities in Raw Copper.—M. Schlagdenhauffen.—After leaving some filings of Chili copper in water for several days, then treating this water (after filtration and slightly acidulating it) with sulphuretted hydrogen, a yellow precipitate was obtained. If carried out on a water-bath, a more abundant orange precipitate was formed. If, after completely exhausting with water, the same sample is treated with potash or with weak hydrochloric acid a considerable precipitate of sulphide of arsenic and sulphide of antimony was obtained in the same manner. Other experiments have given all the indications of the presence of selenious acid and lead.

Series 6, vol. vii., No. 1.

Contribution to the Study of the Glycerophosphates.—A. Astruc.—The author confirms previous observations, that the glycerophosphates of lime in solution are alkaline to methyl-orange, and are sometimes acid and sometimes alkaline to phthalein. To a known volume of a solution of glycerophosphate is added enough sulphuric or hydrochloric acid to give a neutral reaction with methyl-orange; then, with a titrated solution of soda, the quantity of alkali is estimated to give neutrality with phthalein. From this it is easy to deduce the quantity of P_2O_5 contained in the solution. The author concludes that the phosphoric acid in glycerophosphates can be estimated very closely and rapidly by the method he describes; that the glycerophosphates of lime appear to decompose, even during their preparation; and that undecomposed glycerophosphate of lime seems to require a quantity of acid equivalent to that of the soda necessary to act on phthalein in order to react on methyl-orange.

MISCELLANEOUS.

City and Guilds of London Institute.—The students of Finsbury Technical College will hold their Annual Conversazione at the above College on the 18th inst. Dr. Thompson has promised to lecture on "Wireless Telegraphy"; Mr. Innes will give an exhibition of Colour Photography; and Glow-lamp Making will be demonstrated by Mr. Robertson.

International Congress of Hygiene and Demography.—This Congress will be held in Madrid from the 10th to the 17th of April, 1898, under the patronage of H.M. King Alfonso XIII. and H.M. the Queen Regent, and under the presidency of the Minister of the Interior. The two colonial wars in which Spain has been lately engaged have no doubt interfered to some extent with the preliminary work of the Organisation Committee, but the Secretary trusts that this will not interfere with the complete success of the undertaking. The Congress will be divided into two classes:—Class I., Hygiene, subdivided into ten sections; and Class II., Demography, subdivided into three sections. In all of these sections papers will be read, followed by discussions. There will also be an Exhibition in connection with the Congress, divided into ten classes as follows:—(1) Didactic hygiene; (2) Prophylaxis of transmissible diseases; (3) Urban hygiene; (4) Hygiene in relation to dwelling-houses; (5) Hygiene in what refers to exercise and work; (6) Naval and military hygiene; (7) Hygiene of infancy and schools; (8) Food and dressing; (9) Demography and Statistics; (10) Miscellaneous. Persons willing to be registered as exhibitors should should apply to the General Secretary of the Organising Committee, who will immediately refer their requests to the Exhibition Section. Prizes will be awarded consisting of medals and diplomas. The General Secretary is Dr. A. Gimeno, from whom all further information can be obtained.

The Philapelphia Museums.—These Museums had their origin in the successful movement to secure the vast exhibits of natural products from the numerous countries represented at the Chicago Exhibition of 1893. These exhibits were presented to the municipality of Philadelphia, who have devoted a large sum of money to their proper installation. In addition to the Exhibition there is the Scientific and Commercial Library, with its free reading-room, where may be found a large number of statistical and scientific works, valuable to both producers and consumers. A Laboratory has also been started as an adjunct of the Scientific Department of the Philadelphia Commercial Museum, its main object being the examination and analysis of raw materials and manufactured products. The system of this laboratory, which is free to all, will conform closely to that in use in England and on the Continent, and all tests will be made independently in duplicate by two observers, thus ensuring a high standard of accuracy.

MEETINGS FOR THE WEEK.

Monday, 14th.—Society of Arts, 8. (Cantor Lectures). "The Principles of Design in Form," by Hugh Stannus, F.R.I.B.A.

Tuesday, 15th.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.

Wednesday, 16th.—Society of Arts, 8. "The Protection of Industrial Property," by J. F. Iselin, M.A., LL.M.

— Microscopical, 8. "An Essay in Micro-crystallography" (with Lantern Illustrations), by T. C. White. Mr. J. E. Barnard will give an exhibition of Miscellaneous Lantern Slides.

Thursday, 17th.—Chemical, 8. "Some Lecture Experiments," by J. Tudor Cundall, B.Sc. "Observations on the Influence of the Silent Discharge on Electricity in Air," by W. A. Shenstone and W. T. Evans.

— Royal Institution, 3. "Some Italian Pictures at the National Gallery," by Jean Paul Richter.

— Society of Arts, 4.30. "The Plague in Bombay," by Herbert Mills Birdwood, C.S.I., M.A., LL.D. (This meeting will be held in the East Conference Hall, of the Imperial Institute, South Kensington).

Friday, 18th.—Royal Institution, 9. "A Yorkshire Moor," by Prof. L. C. Miall, F.R.S.

Saturday, 19th.—Royal Institution, 3. "The Structure of Instrumental Music" (with Musical Illustrations), by William H. Hadow, M.A., B.Mus.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Normantine.—A correspondent wishes to know if there is a chemical combination or preparation called "normantine."

Erratum.—The paragraph commencing "It is proper," immediately following Table II., p. 49, should follow Table III., p. 50.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 1995.

THE REVIVAL OF ALCHEMY IN FRANCE.*

By H. CARRINGTON BOLTON, Ph.D.

(Concluded from p. 70).

For a student of chemistry to read, digest, and write down in intelligible language, in a limited space, the principles of this new school of chemical philosophers is a difficult task, even for one somewhat familiar with the literature of the ancient alchemists; consequently the following analysis falls far short of the ideal. It is properly the work of a kabalist, a theosophist, and a magician, proud designations which the writer disclaims. The modern alchemists accept all the traditions of their ancient predecessors, but give them a new significance, and interweave the novel phenomena derived from researches in pure science. They claim that during the fourteenth, fifteenth, and sixteenth centuries the official schools of instruction taught exclusively the physical part of the sciences, and that the metaphysical part (which is the real life and soul of the study) has been rejected under the opprobious name of occult science. This living aspect of science has, however, been studied in the secret societies of the initiated, which have preserved the traditions of the kabala, the mysteries of hermetism, and the practice of transmutation. The study of science is as much a religious question as an intellectual one, and worship at an altar should sustain and enlighten the worker in a laboratory. "Chemistry, alchemy, and hermetic philosophy form three steps of the ladder which leads the initiated from the laboratory, through artistic realisation, to the oratory: '*Labora, Opera, Ora et Invenies.*' ".

The modern alchemists also maintain that Darwin and his disciples appreciated but a small part of the great doctrine of evolution, which should be applied to the chemical elements as well as to living beings. The starting point in the evolution of elements is the ether (the universal astral fluid of the kabalist), the infinitely divisible particles of which form chemical atoms by agglomeration. This ether is condensed energy, and hence all matter is resolved into energy.

Energy, matter, and motion form a trinity analogous to the Divine Trinity, one in substance, three in appearance. Matter is one in kind, and the diversity of chemical bodies results from differences in grouping and in motions of the constituent particles. Intelligence is allied in a mysterious way with matter and energy, forming another trinity. Every atom centralises intelligence, is in itself a living entity, and by a process of self-evolution yields the diverse natural bodies. "Ether is the father of hydrogen, from which are derived oxygen, nitrogen, carbon, &c., combinations due to etheric vortices." "Perhaps helium should precede hydrogen." This view of matter as a living entity is greatly insisted on, and the doctrine is called *Hylozoism*. An alchemist who expects to succeed must possess psychic power over atoms, so that by the action of his will they shall group themselves to form the metal desired.

Such is the physical philosophy of modern alchemists; the kabalistic philosophy is by no means so clear, being closely linked to the *Tarot*, which signifies the "hieroglyphs and algebraic calculations of the Primordial Genesis."

Students of the mystical philosophy of the Hebrews discover profound occult significance in accidental similarities of widely differing objects and phenomena. The seven planets, seven days of the week, seven colours, seven orifices in the head, seven metals known to the ancients, seven archangels, and seven infernal demons present to the truly kabalistic mind marvellous and precious analogies. In the "Table of Concordance of Major Arcana" these correspondences are given: "Heth—Justice—Elementary existence—Nizah—Cancer—June—Hydrogen—Fire."

Jollivet-Castelot has written of Kabalistic Alchemy, and a perusal of his essays leaves in the mind of the uninitiated confused memories of colours, numbers, signs of the zodiac, alchemical operations as distillation, fixation, and the like, the names of the sons of Jacob, certain precious stones, geometrical figures, Hebrew characters, Azoth, quintessence, and the Devil, all discussed in a language as obscure as the symbolism portrayed. To conceal esoteric mysteries abbreviations are often used, but one does not have to be very deeply initiated to recognise in P .·. Ph .·. "pierre philosophale," and in G .·. O .·. "grand oeuvre."

Astral light is an important factor in modern hermetism, and is related very closely to the "radiant matter" of chemists and the "ether" of physicists. "Astral light is the universal agent, the universal plastic mediator, the common receptacle of vibrations of motion, and of the phantoms of form."

Writers on modern alchemy discuss the marvels of palingenesis, of homunculi, and of gamahes; they write of the materialisation of a metal through the medium (mediumnité) of a metal; they cite the "Rules of Philalethes," the works of George Ripley and of the Cosmopolite, and refer in the same essay to Berzelius, Berthelot, and Moissan. We are told that "*le diable est le singe de Dieu*," and that the "Cherubim of the Ark of the Covenant symbolises the male and the female of the Universe, the Alchemical Father and Mother," by the very authors who show acquaintance with the most recent advances in pure chemistry. In liquid fluorine they perceive a realisation of the Alkahest, or universal solvent long sought by mediæval alchemists.

Accustomed to juggle with numbers, the kabalist finds abundant opportunity in the atomic weights of the elements, and he makes the most of his opportunity. When the arithmetical sum of the atomic weights of elements entering into a given compound chances to equal the atomic weight of gold, this accidental correspondence is seized upon as a pretext for claiming hermetic relationship between the two substances.

August Strindberg has devoted much study to such correspondence, and points out the following:—

$$K_2MnO_4 = 197 = Au.$$
$$Cu_2Cl_3 = 196 = Au.$$
$$Fe_3S = 197 = Au.$$
$$C_2H_5I + \tfrac{1}{2}Br = 197 = Au.$$

He uses both 196 and 197 as the atomic weight of gold to suit his purposes, and seems to be very weak in arithmetic, for the hypothetical body Fe_3S has a molecular weight of 200.

The ammonium-ferrous-sulphate crystallised with six molecules of water, which chances to have a molecular weight equal to that of gold, is used by Strindberg as basis of the following experiment, which serves to show his method of reasoning and of operating.

Ammoniacal sulphate of iron = 392 = Au is perhaps the solution of the enigma; sulphate of iron (green copperas) precipitates solutions of gold; to precipitate according to monist-chemistry is to enter as a factor into the re-constitution of the body of a compound. Soak a strip of paper in a solution of sulphate of iron, and expose to the fumes of ammonia; the paper will assume a bluish-green colour like that of the protoxide of gold. Dry the strip of paper over a lighted cigar, and the paper will acquire a chestnut-

* Abstract of a Paper read to New York Section of the American Chemical Society, October 1, 1897. From *Science*, N.S., vol. vi., No. 154.

brown colour like that of the deutoxide of gold. Little by little metallic flakes of a golden yellow colour appear, forming a non-solid (*non-fixé*) gold, when the sulphate of iron produces an auto-fecondation by self-precipitation. However, the golden flakes amalgamate with mercury, which property is not shared by iron. After showing by appropriate tests that iron is still present, the hermetic chemist proceeds to explain the reaction by assuming the formation of the hypothetical $Fe_3S=196=Au$, or of the imaginary compound,

$$Fe_2O_3+2H_2O=196=Au,$$

or of the

$$\text{ferrous-ammonium-sulphate}=392=Au_2;$$

and he adds, "The chloride of gold is reduced by the nicotine of the cigar." Since, however, no reagent containing chlorine in any form was used in the experiment, this element must have been created at the same time with the gold, which, however, is "incomplete" gold soluble in unmixed acids.

To acquire knowledge and power for successful hermetic labours, to become eligible for initiation in the occult societies, is no easy task. The aspirant must strive valiantly against the passions that assail him, casting out of his soul pride, anger, jealousy, hatred, avarice, hypocrisy, idleness. If the candidate for honours desires to become worthy of the name hermetic philosopher he must prove himself a Magian; he must learn to exercise his will on matter in all its forms, and to acquire this power he should practice crystal-gazing and reading in magic mirrors; to learn to perceive the invisible he must withdraw from the visible, imposing on himself psychic sleep, called by some hypnosis. As adjuncts to the attainment of the ideal mental state he should use perfumes, music, and light; and eventually the astral body, separated from the physical body, will supply the intellectual, moral, and material illumination indispensable to the Great Work.

It is rather discouraging to learn that, even after fulfilling all these hard conditions, no one can realise the perfection desired uutil he has passed through several of our planetary existences. The would-be alchemist must also follow the percepts of Albertus Magnus; he should be discreet, silent, and must not reveal the result of his labours; he must reside in an isolated place, and choose the time and the hours for his tasks; he must be patient, assiduous, and persevering, and he must be rich enough to bear the expenses of his pursuit. Besides ordinary chemical apparatus he should provide several objects indispensable to his work, a magic wand, a sword to dissolve the astral coagulations, a magic mirror, a brazier for perfumes, a wooden altar covered with a white cloth, and an alchemist's robe of white linen to be worn with a girdle embroidered in gold and silver. In all his chemical operations he must project psychic force into the reagents.

Bright prospects for the future of chemical science are claimed by this school of philosophers. Inorganic chemistry is destined to follow the lines in which inorganic chemistry has prospered; the formation, derivation, or rather the evolution of metalloids (so-called) and of metals will be realised through etheric cyclones, different degrees of condensation of hydrogen. Chemical bodies are of one kind only, and they are all organic and living.

There is a growing belief among advanced chemists in the theory that the elementary bodies as known to us are compounds of a unique primary matter (*protyle*), and that transformation of one kind into a similar one is not beyond the bounds of possibility, but we do not think that the modern hermetists are pursuing the right path to accomplish this end; nor do we believe that the world of science is any nearer the coveted goal of alchemical avarice.

In conclusion, a passage from Lord Bacon: "I was ever of opinion that the philosopher's stone and an holy war were but the rendezvous of cracked brains that wore their feather in their heads."

ON THE DECOMPOSITION OF AURIC CHLORIDE IN DILUTE SOLUTION.

By E. SONSTADT.

It is stated in chemical text-books that solution of auric chloride is decomposed by exposure to light with separation of gold. This reaction I have not obtained, possibly either because my solution was not exposed to light long enough, or because it contained free hydrochloric acid—as ordinary auric chloride, dried on the water-bath, was used. But the same solution which failed to react with moderate exposure to light gave a precipitate of gold on heating for some hours. I then dissolved 1 part of the chloride in about 15,000 parts of water which had been first distilled in the usual way, and was then coloured by addition of a small proportion of bichrome, and again distilled in a glass retort adapted by grinding to a glass receiver, every care being taken to exclude organic matter. The solution behaved on heating exactly as in the former case, gold being precipitated. In both cases a trace of hydrogen peroxide was detected in the solution after the reaction had taken place. If the reaction took place without heating, it is reasonable to suppose that the H_2O_2 produced would be much more easily recognisable.

The reaction appears to be entirely analogous to that which I have shown to take place when platinic chloride is similarly heated in dilute solution (see p. 79; also *Proc. Chem. Soc.*, 1898, p. 25). In the latter case the reaction is expressed by the equation—

$$2PtCl_4+6H_2O=2PtCl+6HCl+3H_2O_2;$$

while the corresponding equation for the auric chloride would be—

$$AuCl_3+2H_2O=AuCl+2HCl+H_2O_2.$$

But as aurous chloride decomposes, as is well known, when heated with water, into gold and auric chloride, gold only is precipitated.

It seems probable that the indicated reaction is a general one for the higher chlorides of metals of the platinum group.

ESTIMATION OF MINERAL MATTER IN RUBBER GOODS.

By L. DE KONINGH.

It is a well-known fact that the amount of mineral matter in rubber goods cannot be determined by means of a simple ignition, as the ash does not represent the original mineral matter. For instance, white-lead becomes lead oxide, chalk is largely reduced to calcium oxide, some oxides volatilise, &c. By using the following process the writer believes he has effected a decided improvement:—Five grms. of the very finely divided sample are treated in a covered beaker with 50 c.c. of fuming hydrochloric acid, and after soaking for an hour the whole is heated up to 70° for another hour; 50 c.c. of water are then added, and the insoluble matter is collected on a filter. The washing with boiling water takes some time, as the acid causes the rubber to swell out to an enormous extent; however, after a litre of water has been used the washings are generally free from acidity. The residue is now carefully transferred from the filter, into a weighed porcelain dish; no practical difficulty will be experienced in this operation. After drying on the open water-bath until no more water-vapour is visible, the dish is placed inside an

air-bath and heated for three hours up to 105°. After cooling it is weighed, and the result is the rubber minus the greater part of its soluble ash. The remainder of the ash is then found by an ignition. Some samples examined by the writer, which gave on simple ignition about 50 per cent of ash, gave only 10 per cent after the acid treatment, and the ash was then found to consist chiefly of barium sulphate. If it be desired to distinguish between heavy spar and silicates, the writer still uses a process described by him some years ago, based on the fact that barium sulphate is soluble in hot sulphuric acid, and may be completely re-precipitated on adding water.

The acid filtrate may, if desired, be subjected to further analysis.

Before recommending the process it was necessary to ascertain if the strong acid dissolves any organic matter. If the filtrate is evaporated nearly to dryness after having added a few c.c. of sulphuric acid, there is obvious darkening, and an unpleasant albuminous odour is noticed. But, as will be seen, the loss is not very great, and may even to some extent be allowed for. Five grms. of a block-rubber containing 40 per cent of ash were treated with 50 c.c. of fuming hydrochloric acid at 70°; 50 c.c. of water were then added, and after standing for several hours 50 c.c. of the filtrate were diluted with 450 c.c. of water, and 30 grms. of crystals of magnesium sulphate were added on account of the presence of hydrochloric acid. Standard solution of potassium permanganate (0·001 grm. oxygen per c.c.) was added until the liquid turned pink, and more was added during the next half-hour; each time the colour began to fade. Three c.c. of permanganate were thus consumed. To ascertain how much organic matter this represents 0·03 grm. of a dry albumenoid (peptone) was dissolved in 25 c.c. of fuming hydrochloric acid, and then titrated with permanganate in exactly the same way; the result was also 3 c.c.

By an easy calculation it follows that 5 grms. of the block-rubber had yielded to the acid about 0·06 grm. of organic matter, or about 1 per cent.—*Journal of the American Chemical Society*, xix., No. 12.

ON SOME NEW COMPOUNDS OF THE CERITE METALS.

By ANDRÉ JOB.

THE oxalates of the cerite metals are soluble in warm concentrated hydrochloric acid. If we let the solution cool slowly to the ordinary temperature, we notice that fairly large, well-defined crystals are deposited. They differ completely in their composition from the original oxalate. In fact, if we calcine them at a red heat and dissolve the residue from the calcination in nitric acid we can perceive the odour of chlorine.

Having made these observations, I was desirous of studying more closely the compound which was formed, and I took the salt of lanthanum as my first subject for analysis. According to my experience the constant composition of the crystals of the oxalochloride is shown by the following formula:—$(C_2O_4)_2Cl_2La_2+5H_2O$.

We can see that it is an oxalate where 1 molecule of oxalic acid has been displaced by 2 molecules of hydrochloric acid. Boiling water decomposes this oxalochloride into insoluble oxalate and soluble chloride:—

$$3[(C_2O_4)_2Cl_2La_2]=2[(C_2O_4)_3La_2]+La_2Cl_6.$$

The crystals obtained as above were kept for several hours at 120° without undergoing any decomposition. At 230° they lose their water of crystallisation. We note the loss of weight. We dissolve in cold nitric acid and precipitate the solution with nitrate of silver, and thus estimate the chlorine. I assured myself that concentrated nitric acid drives off all the chlorine on boiling, and that on evaporating and calcining we obtain a residue of oxide; in this manner I estimated the lanthanum. Finally, I estimated the oxalic acid in the cold in nitric solution, and, in spite of the presence of hydrochloric acid, by means of an oxidising solution of cerium. I shall shortly describe this new method of analysis.

The analysis of this compound does not require the lanthanum to be absolutely free from cerium and didymium. Still I purified the sulphate used as a starting-point with great care. The spectroscope, even, did not show the presence of didymium. I also proved the absence of cerium, for which I have found a new and very sensitive reagent; the salts of the cerite metals are nearly all very soluble in a concentrated solution of neutral carbonate of potassium. One drop of peroxide of hydrogen shows the presence of cerium by an intense red colouration if it is present in any notable quantity, and by as distinct a yellow colour even if the solution is diluted down to 1 part in 250,000.

After having analysed the oxalochloride of lanthanum, I prepared the analogous compounds of cerium and didymium, and made the analyses. I also decided that oxalobromides and oxaloiodides exist. The oxalochlorides of the cerite metals possess one very interesting property; the oxalochloride of lanthanum calcined at a red heat does not lose its chlorine, and the composition of the residue is similar to that of the original oxalochloride, $La_2O_2Cl_2$. Thus we have a convenient method for the easy preparation of the oxalochlorides of these metals.

There is an opportunity to study, from the point of view of chemical equilibrium, the formation of the oxalochlorides in dilute hydrochloric solution. I have observed that the oxalates precipitated from a hydrochloric solution, even when dilute, still retain a considerable quantity of oxalochloride; and thus it may be explained that different chemists, in calcining the oxalates and the sulphates, have constantly found different atomic weights. It remains to be seen if, in starting with oxalochloride itself, we cannot manage to obtain concordant results. I would here recall the fact that Clève prepared an oxalonitrate of didymium, and that Wyrouboff and Verneuil have notified the presence of oxalonitrite of cerium in the oxalate crystallised from a concentrated nitric solution.

I would finally add that Souchay and Leusenn have prepared an oxalochloride of calcium. Calcium presents, in the same manner as the cerite metals, this common property, that its oxalate is insoluble in dilute acids. I am following up the research on the metals whose oxalates are soluble; this will be the subject of another communication.—*Comptes Rendus*, vol. cxxvi., No. 3.

THE PRINCIPAL AMIDE OF SUGAR-CANE.

By EDMUND C. SHOREY.

IT has been more than forty years since Lawes and Gilbert pointed out that in plants used as feed for stock, part of the nitrogen exists in the amide form. Since then several schemes of analysis have been devised by which to determine the amounts of different forms of nitrogen in plants, and numbers of analyses have been published in accordance with these schemes, so that it has come to be generally accepted by chemists that a part of the nitrogen of all plants, in the growing stage at least, is in the amide form. E. Schulze, who has done more than anyone else to advance our knowledge of the forms in which nitrogen exists in plants, states that the amide compounds vary with different plants, and also with the age and condition of the plant.

In 1892 I determined the total and albumenoid nitrogen content of a number of samples of mature sugar-cane. In the samples then examined I found the albumenoid to be about 90 per cent of the total nitrogen. Analyses made later, of another and less mature variety of cane,

showed this non-albumenoid nitrogen to be sometimes as high as 25 per cent of the total nitrogen. The albumenoid nitrogen was determined by precipitating with cupric hydroxide, taking special precautions to prevent any decomposition of the albumenoids by preliminary heating. No attempt was made at that time to determine the character of the non-albumenoid nitrogen.

In January, 1894, a paper was read by W. Maxwell before the Louisiana Sugar Planters' Association on "Organic Solids not Sugar in Cane Juice." The matter of this paper was subsequently issued as a bulletin by the Louisiana Experiment Station. In this paper attention was drawn to the fact already noticed, that all plants contain at some period part of their nitrogen in the amide form—a fact well known to chemists, but apparently overlooked by sugar manufacturers. After giving a number of analyses of cane-juice, in which the difference between the total and albumenoid nitrogen was designated amides, Maxwell stated that the amide of cane-juice was found to be asparagin, crystallised preparations of this body having been obtained. He made, however, no statements regarding the physical or chemical properties of the asparagin obtained, nor did he give any information as to how it was ascertained to be asparagin.

Some months after the publication of this paper, there was a discussion in the *Bulletin de l'Association des Chimistes de Sucrerie*, between H. Pellet and W. Maxwell, as to the possibility of the asparagin of cane-juice affecting the polariscopic reading of such solutions. In view of this possibility I determined to make some preparations of the amide compound or compounds in cane-juice, and ascertain the rotatory power of the same. This work was begun in January and continued until July of last year, and covers every variation in age and condition of cane delivered at the mill last year, as well as some samples of very young cane.

As a result of this work I have found that the principal amide compound present in sugar-cane is *not optically active*, and is *not asparagin*, but glycocoll or glycocin, an amide not heretofore known to occur in plants.

The method of separating the amide was that commonly used, viz., precipitation with mercuric nitrate. To the juice obtained from the cane sample by pressure, a slight excess of lead subacetate was added, the liquid filtered, and to the filtrate an acid solution of mercuric nitrate was added, and the whole brought to faint acidity if strongly acid, by the cautious addition of caustic soda. The precipitate thrown down, which was white and flocculent, after being well washed, was decomposed by hydrogen sulphide. The filtrate from the mercuric sulphide, after being concentrated to a thin syrup, was allowed to stand, when abundant well-defined crystals were generally formed in thirty-six hours. The filtrate from the mercuric sulphide was always quite strongly acid, and the subsequent crystallisation was found to be much more rapid and the yield larger if the solution were neutralised with ammonia before concentration, and neutrality maintained during concentration by the continued addition of ammonia as the solution became acid again. This addition of ammonia made no difference in the character of the crystalline body obtained. The crystals after separation from the mother-liquor were purified by re-crystallising twice.

The mercuric nitrate used was prepared as wanted by boiling mercury with an excess of nitric acid until no further reaction for mercurous nitrate was obtained. I have as yet made no analysis of the white insoluble precipitate which mercuric nitrate gives with the amide body in question.

The purified crystals were in the form of plates or four-sided prisms, belonging to the monoclinic system; glassy in appearance, quite hard, grating between the teeth, and having a sweetish taste. They were soluble in cold water, but much more readily in hot, soluble in 80 per cent alcohol, but insoluble in ether. In all, fifteen preparations of these crystals have been obtained, and in all cases the physical properties of the crystals and the chemical properties of the solution have been the same.

The mother-liquor from the crystals was found to contain other nitrogenous bodies not readily obtained in a crystalline form, the nature of which has not yet been ascertained; but they are comparatively small in amount, and, since nearly the whole of the bodies precipitated from cane-juice by mercuric nitrate can be obtained in a single crystalline form having the properties of an amide, it is quite justifiable to speak of this body as the principal amide of sugar-cane.

In examining this sugar-cane amide to ascertain if it were optically active, solutions containing from 2 to 4 grms. of the substance per 100 c.c. of water were examined in a 200 m.m. tube of a Schmidt and Haensch half-shade polariscope, observations being also made on similar solutions after the addition of caustic soda or nitric acid. In no case was any rotatory power shown. As asparagin is slightly left-handed in water solution, more strongly so in alkaline solution, and strongly right-handed in acid solution, it was at once evident that the sugar-cane amide must be an inactive form of asparagin, or some other body not asparagin. A more extended examination soon brought out other points of difference between the sugar-cane amide and asparagin; and on comparison of the properties of this amide with those of the other known bodies, it was shown unmistakably to be glycocoll.

The chief points of difference between asparagin and the sugar-cane amide may be stated as below:—

	Sugar-cane amide.	Asparagin.
Optical activity.	Inactive.	Left-handed in water solution.
Water of crystallisation.	None.	One molecule lost at 100° C.
Behaviour with Fehling's solution.	Does not reduce on boiling.	Reduces on boiling.
Behaviour when boiled in alkaline solution.	Gives off NH_3 only if alkali is quite concentrated, leaving HCN in solution.	Gives off NH_3, leaving aspartic acid in solution.

It will be noted that these properties of the sugar-cane amide are identical with those of glycocoll, and, in addition to this correspondence, both produced a grey precipitate of metallic mercury when added to a solution of mercurous nitrate, and both give a red colouration with ferric chloride.

The reaction by which the sugar-cane amide is most readily distinguished from asparagin, and by which also its identity with glycocoll is thoroughly established, is that which results on heating in alkaline solution. As is well known, asparagin gives off ammonia when heated in quite dilute alkaline solution, leaving aspartic acid in solution. On the other hand, glycocoll and the sugar-cane amide do not give off ammonia when heated in alkaline solution unless such solution be strongly alkaline, and after the evolution of ammonia has ceased no aspartic acid is found in the solution, but if hydrochloric acid be added to acidify and the solution heated, hydrocyanic acid is given off and can be detected by the smell, and oxalic acid is left in solution and can be precipitated as calcium oxalate. When operating with very small quantities of the amide, as I often found it necessary to do, the quantity of hydrocyanic acid given off in this reaction is so small that the smell is masked by that of the hydrochloric acid; in this case the presence of hydrocyanic acid can be established in the usual way by placing a drop of yellow ammonium sulphide on a porcelain dish, holding over the boiling solution for a few seconds, removing the excess of sulphide by blowing, and proving

the presence of a thiocyanate by the red colouration produced on addition of ferric chloride.

The sugar-cane amide also gives off hydrocyanic acid when heated with dilute sulphuric acid and manganese dioxide.

When heated in a sealed tube with benzoic acid, the sugar-cane amide gives hippuric acid, a condensation characteristic of glycocoll, and one by which it is supposed hippuric acid is formed in the animal body.

The hippuric acid so formed was identified by separating it from any remaining benzoic acid by agitation with petroleum ether, evaporating the insoluble residue to dryness with nitric acid and heating, when the characteristic smell of nitrobenzol was detected.

Glycocoll has been prepared in the usual way from hippuric acid by boiling with dilute sulphuric acid, and the reactions given above as characteristic of that body have been verified throughout.

It having been thus thoroughly established that the principal amide of sugar-cane is glycocoll, it is well to note that there are certain points in which glycocoll resembles asparagin, and the resemblance is such that anyone prone to jump at conclusions would, on obtaining a crystallised preparation of the sugar-cane amide, immediately pronounce it asparagin. The points of resemblance are these:—First, the general appearance, solubility, &c., of the crystals; second, neither gives up any nitrogen when treated with sodium hypobromite in alkaline solution; third, both dissolve cupric hydroxide to a blue solution; and fourth, both contain the same per cent of nitrogen. Asparagin crystallised with 1 molecule of water of crystallisation and glycocoll each contain theoretically 18·66 per cent nitrogen, while the average of all samples of the sugar-cane amide was 18·69 per cent. The Gunning method was used in determining the nitrogen, and clean, well-defined crystals were selected for such determinations.

In all, fifteen preparations of the glycocoll have been made from sugar-cane; and the samples of cane from which it has been prepared have included young shoots of cane a few weeks old, the green tops of cane one year old, and mature cane growing at elevations from 400 to 1200 feet above sea-level. It is fair, then, to conclude that glycocoll is not only the principal amide of sugar-cane, but is also a normal constituent of this plant at all periods of its growth.

I have as yet made no attempts to estimate the quantity of glycocoll in sugar-cane or any of its products, but have noticed that larger amounts have been obtained from young than from mature cane.

The average nitrogen content from mature sugar-cane is probably about 0·30 per cent, and of this at least 0·22 per cent is albumenoid nitrogen; so that the amido content cannot be higher than 0·08 per cent, and probably is often less than 0·02 per cent. It is easily seen, then, that the preparation of any quantity of the sugar-cane amide entails considerable labour, and this, coupled with the fact that this work has been done at odd times during a busy grinding season, is my excuse for the incompleteness of this research in some respects.

The identification of glycocoll, glycocine, or amido-acetic acid in sugar-cane is of interest from several points of view. Its occurrence has not been noted in a plant before, and it has been considered a body belonging wholly to animal chemistry. It can be prepared from gelatin by heating with acids or alkalies,—in fact was first prepared in this way,—and it has been supposed that it was formed in the animal body from gelatin or gelatin-yielding proteids.

It does not seem to occur free in the animal body, and the theory of its formation from proteids seems to have been demanded by the following fact:—Benzoic acid, when taken into the stomach, appears in the urine as hippuric acid, and to explain this it has been supposed that the condensation already referred to takes place, viz., benzoic acid and amido-acetic acid combine to form hippuric acid with the elimination of water:—

$$C_6H_5COOH + CH_2NH_2COOH = \\ = C_6H_5CONHCH_2COOH + H_2O.$$

This view is strengthened by the fact that when glycocol is taken with benzoic acid the yield of hippuric acid is increased.

In the urine of herbivorous animals hippuric acid occurs in relatively large quantities, and while the food of such animals has been deemed capable of supplying the benzoic acid part, the source of the glycocoll to form such large quantities of hippuric acid has been more or less of a puzzle to physiologists.

The identification of glycocoll in sugar-cane, and the fact that it has been mistaken for asparagin, suggests the probability of its occurrence in other plants, especially the *Gramineæ*, which form the major part of the food of herbivorous animals; and it is quite likely that the source of the hippuric acid in the urine of such animals will be found in such occurrence.

In vegetable, as in animal physiology, the question of the constitution of proteids is uppermost. Now glycocoll in the physiology of sugar-cane no doubt plays the same part which other amides are known to do in other plants. It is the form in which nitrogen is conveyed to growing parts, and when maturity is reached the amide becomes the albumenoid to become the amide again when a new growth takes place. A number of facts collected during this study of the sugar-cane amide point to the existence in cane of a gelatin or gelatin-yielding proteid which yields glycocoll as one of the products of decomposition. This, coupled with the well-known and comparatively simple constitution of glycocoll, seems a step toward the understanding of at least one proteid of sugar-cane. The further study of this matter promises to be of special interest, both from a physiological and a technical point of view.

From the sugar manufacturer's point of view the presence of glycocoll presents the following points of interest:—It is known that at various stages of sugar manufacture ammonia is given off from boiling cane-juice, especially if this juice has been rendered alkaline by an excess of lime. This has been stated as due to the decomposition of asparagin into aspartic acid and ammonia. But since we know that the amide is glycocoll and not asparagin, and that glycocoll is not decomposed unless boiled in strongly alkaline solution, it is plain that the ammonia must be derived from the decomposition of albumenoids. When, as is generally the case, cane-juice is maintained approximately neutral throughout the course of manufacture, the whole of the glycocoll originally present in the juice should be found in the final molasses.

Whether this theory always carries out in practice I have not yet ascertained, but I have obtained glycocoll in comparatively large quantities from several samples of refuse molasses by the same method by which it was obtained from cane juice.

In one sample I determined the amounts of different forms of nitrogen according to a well-known scheme of analysis with the following results:—

	Per cent.
Nitrogen as free ammonia	0·011
„ albumenoids	0·126
„ peptones	0·050
„ amides	0·201
„ other forms	0·228
Total nitrogen..	0·616

Free ammonia was determined by distilling with magnesia free from carbonate, and albumenoids by precipitating with cupric hydroxide. The nitrogen designated peptones is that precipitated by phosphotungstic acid after the removal of free ammonia and albumenoids. In the case of cane juice and its products this precipitate

does not contain peptone bodies, and its character will be treated in a future paper. After removal of these three forms of nitrogen, amides were determined by boiling for an hour with 2 per cent sulphuric acid, neutralising, and distilling with magnesia free from carbonate and doubling the amount of ammoniacal nitrogen obtained for amide nitrogen. This method, which is fairly accurate in the case of asparagin (which gives up half its nitrogen as ammonia when boiled with dilute acids), is of no value in the case of glycocoll, so that the above analysis should read—Amides and other forms, 0·429 per cent, instead of

	Per cent,
Amides	0·201
Other forms	0·228

From a number of years' experience in working with cane juice, I am convinced that the formation of molasses is due to mechanical, rather than chemical, conditions, that the presence of viscous non-crystallisable bodies presents the further crystallisation of sugar by rendering the motion of the sugar molecules in the liquid difficult, and the mellassigenic action of crystallisable salts is very slight. A body such as glycocoll would then exert little effect on the crystallisation of sugar one way or the other, especially as it exists in cane in such small amounts, but it is likely that the proteid directly connected with glycocoll will be found to be highly melassigenic.

We have been in the habit of associating the so-called gums or viscous bodies in cane juice with the cellulose or non-nitrogenous constituents of the plant, but we may have to modify this view in the presence of a gelatin-yielding proteid peculiar to sugar-cane and allied plants. —*Journal of the American Chemical Society*, xix., No. 11.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 3rd, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Charles Baskerville, North Carolina University, Chapel Hill, North Carolina; Alfred Campion, 637, Alexandra Parade, Dennistown, Glasgow; Robert Martin Caven, University College, Nottingham; F. Hudson-Cox, 67, Surrey Street, Sheffield; John Arnold Fleming, Britannia Pottery, Glasgow; Harry Pearson Hodgson, Caldew Bank, Cummersdale, Carlisle; Edwin Charles Jee, 45, Pepys Road, New Cross, S.E.; Edward Jones, Vine Cottage, Tudor Road, Kingston-on-Thames; Walter Ratcliffe, 21, Mawdsley Street, Bolton; Henry Somerville, 33, Vincent Square, S.W.; Harry St. John, Thornfield, Sunderland.

Of the following papers those marked * were read:—

*8. "*The Volumetric Estimation of Sodium.*" By H. J. H. FENTON, M.A.

Dihydroxytartaric acid, in presence of dilute sulphuric acid, is readily oxidised by potassium permanganate at the ordinary temperature, the reaction affording a very convenient method for the estimation of the acid or its salts. A method has been devised for the quantitative estimation of sodium based upon this relation and upon the sparing solubility of sodium dihydroxytartrate. The solubility of the sodium salt at 0° is shown to be extremely small, and in presence of excess of a dihydroxytartrate is practically negligible.

The substance to be examined, in concentrated neutral solution, is mixed with excess of potassium dihydroxytartrate, and the mixture is kept at 0° for half an hour. The precipitated sodium salt is washed with a little ice-cold water, dissolved in excess of dilute sulphuric acid and titrated with potassium permanganate.

The results obtained with sodium sulphate, chloride, nitrate, acetate, and with rochelle salt, are accurate within 0·3 per cent. The presence of magnesium does not interfere with the accuracy of the results; but ammonium salts, if present in excess, lead to low results. Full details for working the process are given in the paper.

The potassium and ammonium salts of dihydroxytartaric acid have been prepared and examined, and, together with other derivatives of the acid, will be described in a future communication.

DISCUSSION.

Mr. HEHNER said that analysts would welcome the method. It was remarkable that sodium, the most widely distributed element, had hitherto been without a direct method of quantitative estimation. He would suggest that the process should be conducted gravimetrically.

Mr. JOHN A. R. NEWLANDS said that in some experiments for manufacturing purposes, made a quarter of a century ago, he had used a method in which sodium was precipitated as acid oxalate, using suitable precautions, and afterwards titrated, either before or after incineration. The results, however, were only of an approximate character, and did not approach in accuracy to those obtained by the author of the present paper.

Dr. LAWSON asked how Mr. Fenton's method for the production of dioxytartaric acid compared, as regards yield, with that usually employed. The sodium salt was of technical importance in the preparation of a valuable dye-stuff, and it would be of interest to know whether the results were comparable with those obtained by decomposing nitrotartaric acid.

Mr. FENTON, in reply, said that he had suggested in the paper that the process might be conducted gravimetrically, but he considered that the volumetric method would find most favour. He had experimented with other sparingly soluble sodium salts, but did not think that any could nearly compare with the dihydroxytartrate as regards insolubility. In reply to Dr. Lawson, he said that the process possessed many advantages as compared with the usual method of preparing the sodium salt from nitrotartaric acid.

*9. "*The Atomic Weight of Boron.*" By F. P. ARMITAGE.

The determination of the water of crystallisation was the method used. The values for the ratio $Na_2B_4O_7 : H_2O$ obtained by previous workers are not sufficiently concordant to allow of the values for the atomic weight of boron, calculated from them, being regarded as very trustworthy. The discrepancies are probably to be traced to the slight efflorescence which occurs during the preliminary drying of the crystals of borax. A new method of drying was consequently applied, the borax being washed with alcohol and ether successively, and the ether expelled by exposure for six hours in a vacuum. A given weight of the dry crystals was dehydrated in a stream of air, the final traces of water being expelled by fusion over the Bunsen burner and not over the blowpipe.

In a series of six experiments, the greatest difference in the percentage value for the water of crystallisation was 0·413, and the mean atomic weight of the element as calculated from these values 10·959, a number differing by 0·006 from that recently obtained by Ramsay and Aston in their experiments on the distillation of sodium diborate with hydrochloric acid and methyl alcohol.

Certain results are also given in which the method of titration (*c.f.* Rimbach, *Ber.*, 1893, xxvi., 164) is applied with a view of ascertaining the possible degree of its accuracy. Thus, a given weight of fused borax was dissolved in water and titrated with dilute sulphuric acid, the strength of which had been determined (i.) by titration with solution of pure soda of known strength, (ii.) as barium sulphate. The value 10·928 was obtained for the

atomic weight of boron as a mean of two experiments performed by this method.

Discussion.

Mr. Veley said that methods of determination of atomic weights based upon the elimination of water from a crystalline salt presented the difficulties, firstly, of the mechanical inclusion of water within the walls of the crystals, however fine; and secondly, of the possible efflorescence and deliquescence of such salts. These difficulties, as also that of the intumescence of the anhydrous salt, when heated with the blowpipe, induced Ramsay and Aston to reject this method. It appeared that the author had overcome these difficulties to a great extent by removing the adherent water by washing with absolute alcohol and subsequently with ether, which was pumped off, as also by heating the anhydrous salt only at a temperature obtained by the Bunsen burner, and not at that of the blowpipe, when loss occurred either on account of the volatilisation or the decomposition of the borax. The experiments of the author also showed that the method of determining the atomic weight proposed by Rimbach, though not of the degree of exactitude necessary for such determinations, was probably more accurate for the purpose of acidimetry than that of sodium carbonate, which was not readily obtained of the composition required by its molecular formula.

Mr. Groves asked whether the volatilisation observed when the crucible was heated in the blowpipe flame might not be due to the action of water vapour and carbonic anhydride which would diffuse through the perforated cover.

Dr. Scott was astonished that anyone now should attempt to determine atomic weights through calculations of the amount of water of crystallisation contained in hydrated salts. The experiments of J. W. Mallet on ammonia alum, and of many other experimenters, had shown how unsatisfactory such determinations must always be. It was evident that as such salts produced a determinate vapour pressure of water depending on the temperature, if the air in which they were dried contained less than that amount the salt must lose water during its drying.

The President considered it superfluous to record weighings to six places and the atomic weight to three places of decimals, having regard to the method adopted. With reference to the process employed by the author in drying the borax, he failed to understand why, if borax is an efflorescent salt, it loses no water of hydration when washed with absolute alcohol. He suggested that in investigating this point the influence of time should be taken into account.

Mr. Armitage, in reply, said that he had not examined the sublimate formed on the lid of the crucible when ignited with the blowpipe, as his object was to show merely that a loss of weight would occur if this method is adopted. The standard of atomic weight taken was oxygen = 16. The time occupied for each washing by absolute alcohol was three to four minutes.

*10. "*Rate of Escape of Ammonia from Aqueous Solution.*" By E. P. Perman, D.Sc.

If a current of air is drawn through a dilute aqueous solution of ammonia at a uniform rate, the amount of ammonia q in solution when a volume V of air has passed through the solution, is accurately represented by the equation $\log q = a - bV$, a and b being constants. The volume of air was measured by a meter.

The equation does not express the results given by a concentrated solution; the solution used in most of the experiments contained 70 grms. of ammonia per litre.

A number of experiments, conducted at different temperatures, prove that the logarithmic formula holds good between 0° and 46°; it was also found to hold good when the pressure was varied.

The value of b is a measure of the rate of escape of the gas from the solution under any specified conditions; such values were obtained at various temperatures, and a simple connection was found between b and temperature $t°$, viz., $\log b = \alpha + \beta t$, α and β being constants. Combining the two logarithmic equations,—

$$\log q = a - y, \text{ if } \log y = \alpha + \log V + \beta t.$$

From this expression the amount of ammonia left in a solution after a certain volume of air has been drawn through it can be at once calculated, provided that, at the beginning of the aspiration, the strength of the solution was not much greater than that mentioned above.

Discussion.

The President remarked that the subject investigated by the author was a very complicated one. He thought that the variations in the tension of the ammonia solution used in the experiments should be determined, as a valuable addition to the paper. It was probable that the results would be expressed by the equation—$\log p = A - B/T$—where A and B are constants and T is the absolute temperature, which was applicable to many similar cases.

Dr. Perman, in reply to a question by Mr. Groves, stated that the conditions of volatilisation of ammonia from the solution had been varied by using flasks of different capacities and tubes of different diameters. In reply to Dr. Wilderman, he said that he considered that his results confirmed Henry's law for ammonia in dilute solution. In reply to the President, the author said he had found approximately the vapour-pressure of the ammonia solution used in most of the experiments at a temperature of 20°; it was about 70 m.m., although he had not found the vapour-pressure of solutions of different strengths, but intended to do so. He regarded the method of expressing the results given in his paper as the most convenient for the present, though as yet it was only empirical.

11. "*On the Dissociation of Platinichloride in Dilute Solution; and the Production of Platinum Monochloride.*" By E. Sonstadt.

A solution of potassium platinichloride in 1000 parts of water undergoes no sensible change on heating for an hour or two. But a solution in 10,000 parts of water becomes turbid almost immediately on heating, and the turbidity increases until, after some hours, the liquid becomes nearly opaque. On continuing the heating for some days, water being added from time to time to maintain the bulk, a sediment forms and the liquid partially clears. By increasing the quantity of water during the heating, the clearance is facilitated. The reactions that take place are, first, the dissociation of the potassium platinichloride;

$$(1)\ K_2PtCl_6 = 2KCl + PtCl_4,$$

and then the decomposition of the platinic chloride, with formation of platinum monochloride (PtCl or Pt_2Cl_2), hydrochloric acid, and hydrogen peroxide, thus:—

$$(2)\ 2PtCl_4 + 6H_2O = 2PtCl + 6HCl + 3H_2O_2,$$

The yellow non-crystalline precipitate of hydrated platinum monochloride is difficult to collect, for it passes through the filter until the pores are clogged, and then the filtration is exceedingly slow. The precipitate should not be dried on the filter, but washed off, as far as possible, into a dish, and the water evaporated. When dried on the water-bath, the salt is brown; it still retains water, the last traces of which can scarcely be expelled before incipient decomposition begins; the anhydrous salt is black, or nearly so.

The clear filtrate, when concentrated, is strongly acid, and on drying and dissolving the residue in a little water, potassium chloride may be crystallised out. There is also a small proportion of potassium platinichloride, which may be either a portion of the original salt that has escaped decomposition, or may have been formed by a reverse action due to solution of the monochloride in the hydrochloric acid set free as described, in presence of hydrogen peroxide and air.

The hydrated salt, when treated on the water-bath with strong soda solution, turns brown, and dissolves to a slight extent. But the brown residue is only partly dehydrated, and recovers its original colour after washing and exposure. The soda solution deposits the unchanged salt on dilution and long exposure to the air. It dissolves readily in hydrochloric acid; slightly in hot dilute sulphuric acid, apparently without decomposition; in moderately dilute nitric acid, used in large proportion, it dissolves to a deep brown liquid, which, evaporated to dryness on the water-bath until no acid odour is perceptible, leaves a dark brown residue. This dissolves in hot water to a clear dark brown liquid, which, on further heating, suddenly deposits the whole of the original salt, less any impurities present, which remain in the solution. The precipitate, when collected on a filter, is deeper coloured than before, being of an orange tint. The filtrate is free from platinum; but on continued washing with water, the salt dissolves slightly, and the filtered liquid becomes clouded.

Advantage was taken of this process of purification to obtain the monochloride for analysis. An attempt to analyse about 0·1 grm. of the salt partially failed, owing to the presence of impurities taken up from the enormous proportion of distilled water used in its preparation. The monochloride, purified as described, was washed into a dish, and after drying on the water-bath, was transferred to a small porcelain crucible. The salt weighed 0·2575 grm. The crucible was cautiously heated, with frequent application of the cold lid. Traces of nitric acid came off as well as water. When moisture ceased to be given off, the salt weighed 0·2315 grm. It was then more strongly heated, when chlorine came off, and a final trace of water. The heat was then raised until the decomposition was complete. The platinum obtained weighed 0·1945 grm., which corresponds to 0·229 PtCl, a result which may be considered fairly satisfactory.

It might be supposed that platinic chloride itself, instead of dissociating from potassium chloride as in the described process, would be preferable, when it is desired to obtain platinum monochloride. But the presence of free acid in the best-dried specimens of platinic chloride renders it unfit for the purpose. A specially dried specimen of platinic chloride dissolved in 10,000 parts of water gave a barely perceptible reaction. With 15,000 parts of water, after heating for some hours, the liquid became turbid, and gave a slight deposit, but not equivalent to that obtainable from a corresponding solution of potassium platinichloride. If, however, a solution of platinic chloride be evaporated on the water-bath with nitric acid, the residue dissolved in water, and the solution evaporated again two or three times, the platinic chloride is not appreciably decomposed, but retains a little nitric acid instead of the hydrochloric acid with which it is otherwise associated. A solution of platinic chloride thus prepared, heated in 5000 parts of water, gives a distinct turbidity, but the reaction is more nearly complete with double that proportion of water. The precipitate differs slightly in its properties from that obtained from the potassium salt; it is of a deeper tint, and is but slightly soluble in nitric acid. When treated with nitric acid and the solution evaporated over the undissolved portion, a weak solution only is obtained on adding water, which, on concentrating, deposits the salt, but not instantaneously. After evaporating the aqueous solution, the hydrate of platinum monochloride is insoluble in water, except, as in the former case, on continued washing. A specimen of the hydrate thus obtained weighed after drying on the water-bath, 0·1700 grm.; when anhydrous, it weighed 0·1549 grm., and after expulsion of the chlorine by ignition 0·1316 grm. of platinum remained. Theory requires from this quantity of platinum 0·1552 grm. PtCl.

The potassium platinichloride used in the experiments had been several times re-crystallised, and was perfectly free from acid. The yield of platinum monochloride was about five-eighths of that theoretically obtainable.

The author has made some experiments with the view of directly proving the presence of hydrogen peroxide in the liquid, though, considering the conditions of dilution and temperature, the quantity present at any time must be exceedingly small—the total amount produced according to the equation, assuming the reaction to be complete, being in the proportion of from 1 : 100,000 to 1 : 150,000 to the liquid present. In a solution that had been heated for five days, the author, using the chromic acid and ether test, obtained a faint colouration, hardly visible except to an observer of great sensitiveness. The author then prepared a solution in about 15,000 parts of water of some very pure crystals of potassium platinichloride (a previous trial with a salt of only ordinary purity having failed), and heated the solution for several hours at a temperature slightly below 70°. There was only a slight turbidity, for the temperature was too low for good progress. On testing the solution the next day, a faint bluish tint in the ether was perceptible. That hydrochloric acid is a product of the reaction was proved as follows:—A hot strong solution of potassium platinichloride was poured into a large quantity of a nearly saturated solution of pure potassium chloride. The precipitated platinichloride was collected, well washed with water, and afterwards with alcohol, and dried on the water-bath. A solution of about one part of this salt to 10,000 of water was heated for five days, the precipitate allowed to settle, and filtered off. A portion of the solution was concentrated in an open dish to about one-fifth of its bulk, and was then distilled. Silver nitrate added to the distillate gave a precipitate of silver chloride insoluble in nitric acid.

12. "*Effect of the Mono-, Di-, and Tri-chloracetyl Groups on the Rotatory Power of Methylic and Ethylic Glycerates and Tartrates.*" By PERCY FRANKLAND, F.R.S., and THOMAS STEWART PATTERSON, Ph.D.

With a view of ascertaining the rotatory effect of the halogens when attached at a point in the molecule remote from the asymmetric carbon atom, the authors have introduced the mono-, di-, and tri-chloracetyl groups into the methylic and ethylic tartrates and glycerates. This was effected by acting in each case with the acid chloride on the ethereal tartrate and glycerate respectively. The acid chlorides were in all cases prepared by heating the halogen-substituted acetic acid with phosphoric anhydride in a current of hydrochloric acid. Two acidyl groups were in all cases introduced, excepting in that of trichloracetyl, of which only one equivalent could be made to substitute in methylic and ethylic tartrates, whilst two equivalents reacted with the corresponding glycerates.

The rotations were in all cases determined at several different temperatures, so as to ascertain the influence of the latter.

The results are summarised in the accompanying table.

Methylic and ethylic di-monochloracetyltartrates have also been prepared by Freundler (*Bull. Soc. Chim.*, 1895, [3], xiii., 1055—1063), who only obtained them as liquids with the following rotatory powers:—

Methylic di-monochloracetyl tartrate $[\alpha]_D^{18°} = +3·5°$

Ethylic " " $[\alpha]_D^{15°} = +9·4°$

In consequence of this discrepancy between Freundler's results and those of the authors, these two compounds have been prepared again (see next abstract), with the result that the authors' figures have been confirmed.

13. "*The Rotation of Ethylic and Methylic Di-monochloracetyltartrates.*" By PERCY FRANKLAND, F.R.S., and ANDREW TURNBULL, Ph.D.

The ethylic compound has been again twice prepared by the authors, using different proportions of monochloracetylchloride and ethylic tartrate:—

First preparation, $[\alpha]_D^{20°} = +7·90°$

Second " $[\alpha]_D^{20°} = +7·76°$

	$[\alpha]_D^{15°}$	$[\alpha]_D^{100°}$	
Methylic glycerate	−4·80°	−8·31° *	(calculated).
„ diacetylglycerate	−12·04	−19·24*	(calculated).
„ di-monochloracetylglycerate	−12·91	−17·99	b. p. 197° (15 m.m.); m. p. 43—44°.
„ di-dichloracetylglycerate	−13·96	−17·18	b. p. 207° (20 m.m.).
„ di-trichloracetylglycerate	−14·20	−15·30	b. p. 199—200° (15 m.m.).
Ethylic glycerate	−9·18	−12·55*	(calculated).
„ diacetylglycerate	−16·31	−23·09*	(calculated).
„ di-monochloracetylglycerate.	−16·80	−22·08	b. p. 198° (15 m.m.).
„ di-dichloracetylglycerate	−18·20	−21·10	b. p. 203° (15 m.m.).
„ di-trichloracetylglycerate	−18·70	−18·40	b. p. 202° (15 m.m.).

	$[\alpha]_D^{20°}$	$[\alpha]_D^{100°}$	
Methylic tartrate	+2·14°	+5·99°	m. p. 48°.
„ diacetyltartrate	— †	—	m. p. 103°.
„ di-monochloracetyltartrate	−0·62	+2·57	b. p. 217° (18 m.m.); m. p. 55°.
„ di-dichloracetyltartrate	+11·9	+10·9	b. p. 220—221° (15 m.m.); m. p. 64—65°.
„ mono-trichloracetyltartrate	+8·4	+10·15	m. p. 79—80°.
Ethylic tartrate	+7·66	+13·29	
„ diacetyltartrate	— ‡	—	m. p. 66·5°.
„ di-monochloracetyltartrate§	+7·67	+11·81	b. p. 217° (15 m.m.): m. p. 27°.
„ di-dichloracetyltartrate	+16·3	+17·08	b. p. 225° (15 m.m.).
„ mono-trichloracetyltartrate	+15·5	+17 6	b. p. 185° (16 m.m.).

* These values for $[\alpha]_D$ at 100° for methylic and ethylic glycerates and diacetyl glycerates have been calculated from the data given in a paper by P. Frankland and MacGregor (*Trans.*, 1894, lxv., 768).

† $[\alpha]_D^{25°} = -15·1°$ (in absolute alcoholic solution).

‡ $\alpha_D = +5°$ ($t=25$, $l=1$).

§ See next abstract.

The substance subsequently crystallised (m. p. 27°), after which the rotation $[\alpha]_D^{20°} = +7·61°$ was found.

The methylic compound was also prepared and again gave the m. p. 55°; the rotation was $[\alpha]_D^{20°} = -0·68°$.

Thus the results obtained with both compounds by one of the authors (see previous abstract) were confirmed, whilst additional evidence of their accuracy was afforded by the ethylic compound being obtained in the crystalline state.

Ethylic mono-monochloracetyltartrate in a state approaching purity was also prepared, and it was found to possess a considerably higher dextro-rotation than the corresponding di-acidyl compound, thus $[\alpha]_D^{20°} = +11·44°$.

It is, therefore, inferred that the higher figures obtained by Freundler may have been due to the presence of mon-acidyl compounds, and this is borne out by the lower densities and boiling-points which he records.

PHYSICAL SOCIETY.

Annual General Meeting, February 11th, 1898.

Mr. SHELFORD BIDWELL, President, in the Chair.

THE Report of the Council was read by Mr. Elder.

Dr. ATKINSON then presented the Treasurer's Report, and informed the Society of the improved condition of its finances. The difficulties of the previous year had arisen from the expenses incurred by the publication of Abstracts of current scientific literature; these difficulties had been surmounted without drawing upon the Reserve Fund. Very few Fellows had objected to the increase of subscription. In acknowledgment and appreciation of the Abstracts, now presented to all Fellows, many of the original Life-members had lately made additional voluntary donations to the funds of the Society, thus sharing with new Fellows the extra outlay involved by the Abstracts. It was to be hoped that all Life-members would adopt this course, more especially as the scope of scientific literature covered by the Abstracts was now being extended to British as well as to foreign sources.

Votes of thanks were passed to the Council, the Officers, and to the Council of the Chemical Society for the use of their rooms at Burlington House.

Two Honorary Fellows were unanimously elected by ballot, *i.e.*, Riccardo Felici, Professor in the University of Pisa; and Emelio Villari, Professor in the University of Naples.

Council and Officers for the forthcoming year were elected as follows:—

President—Mr. Shelford Bidwell.

Vice-Presidents, who have filled the Office of President—Dr. J. H. Gladstone, Prof. G. C. Foster, Prof. W. G. Adams, The Lord Kelvin, Prof. R. B. Clifton, Prof. A. W. Reinold, Prof. W. E. Ayrton, Prof. G. F. Fitzgerald, Prof. A. W. Rücker, Capt. W. de W. Abney.

Vice-Presidents — Prof. C. Vernon Boys, Maj.-Gen. E. R. Festing, Mr. G. Griffith, Prof. J. Perry.

Secretary—Mr. H. M. Elder, 50, City Road, E.C.

Foreign Secretary—Prof. S. P. Thompson.

Treasurer—Dr. E. Atkinson.

Librarian—Mr. W. Watson.

Other Members of Council—Prof. H. E. Armstrong, Mr. Walter Baily, Mr. L. Clark, Dr. A. H. Fison, Mr. R. T. Glazebrook, Prof. A. Gray, Prof. J. Viriamu Jones, Mr. S. Lupton, Prof. G. M. Minchin, Mr. J. Walker.

The PRESIDENT then read an Address, in which the aims and history of the Physical Society were outlined. This Address will be published in full in due course.

Prof. RÜCKER said that, among the new and useful departures lately made by the Physical Society, the institution of a Presidential Address was particularly worthy of notice; it was very desirable, from time to time, to hear a summary of what had been achieved during the year; it was also desirable that the objects of the Society should be, from time to time, definitely stated: this departure had been fully justified by the Address of Mr. Shelford Bidwell.

A paper by Mr. G. H. BRYAN, on "*Electro-magnetic Induction in Plane, Cylindrical, and Spherical Current Sheets, and its Representation by Moving Trails of Images*," was read by Mr. ELDER.

The phenomena of induction in a cylindrical conducting

sheet in a two-dimensional field, and of induction in a spherical sheet in any field due to the generation or motion of poles, magnets, or currents, in the presence of the sheet, can be represented by moving trails of images which are but slightly more complicated than the well-known trails of images in a plane sheet. The images, representing the potentials of the induced currents on the two sides, start from the source of disturbance and its inverse point, and move normally away from the surface of the sphere and cylinder, with velocity varying directly as the disturbance. At the surface of the sheet this velocity becomes equal to the corresponding velocity for a plane sheet. The images are in most cases similar in nature to the inducing source of disturbance, and their intensities are found, in every case, to vary as a power of the distance from the centre. The images due to the sudden generation of a magnetic pole in the presence of a spherical sheet are, however, analogous to the hydrodynamical image of a source in a sphere.

Dr. S. P. Thompson said the method and the results obtained would find useful application in the solution of many allied problems.

The President proposed a vote of thanks to the author. The meeting was then adjourned until Saturday, February 26th, on which occasion the Physical Society will visit Eton College.

Fellows are informed that a train leaves Paddington for Windsor at 2.25 p.m.; this arrives in time for the meeting, which is at 4 p.m.

ROYAL INSTITUTION.

General Monthly Meeting, February 7th, 1898.

Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members:—E. Cortes, J. S. Fairfax, S. Fisher, G. Humphreys-Davies, O. Imray, J. W. Jarvis, J. Levinstein, J. S. MacArthur, The Right Hon. Lord Monk Bretton, F. J. Quick, E. Riston, C. Samson, Mrs. R. L. Smith, and Rear-Admiral A. K. Wilson, V.C., C.B.

The special thanks of the Members were returned to Mrs. Tyndall for her liberal donation of £1000, presented in the name of the late Dr. John Tyndall, D.C.L., F.R.S., for the Promotion of Science. Thanks were also returned to Sir Frederick Abel, Sir Andrew Noble, and Professor Dewar for donations to the Fund for the Promotion of Experimental Research at Low Temperatures.

It was announced that the Centenary of the Royal Institution would be celebrated next year.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Monday, January 31st, 1898.

Dr. Bolam in the Chair.

Dr. Macdonald read a paper discussing the Hydrogenation of Terephthalic and Phthalic Acids, by v. Baeyer, and of Naphthols and Napthylamines by Bamberger.

The work of these investigators shows that the characteristic properties of aromatic compounds are due to the symmetry of the double bonds in the molecule. As soon as a ring loses this symmetry by hydrogenation, it ceases to possess aromatic and assumes fatty properties. Baeyer's results are of unique importance in showing that maximum stability is conditioned by a symmetrical disposition of the double bonds in the molecule. Thus the dihydroterephthalic acids $\Delta^{2,5}$ and $\Delta^{1,5}$ readily pass into $\Delta^{1,4}$, the most symmetrical form. Again, the most stable dihydrophthalic acid, $\Delta^{2,6}$, is the most symmetrical; and the least symmetrical hydrophthalic acids, $\Delta^{2,5}$, $\Delta^{1,3}$, and Δ^{3}, are either incapable of existence or exist only under the most favourable conditions.

In the light of the easy transposition of these compounds and from considerations of energy and elasticity and perfect symmetry of the benzene molecule, we could not expect that two ortho-di-derivatives of benzene could possibly exist, at least under any but the most extraordinary conditions.

Dr. Dobbin then read a short review of Professor Oscar Loew's book entitled "The Energy of Living Protoplasm" (a reveiw of this book has already appeared in the Chemical News, vol. lxxiv., p. 255). His primary object in doing so was to call the attention of the members to the existence of the book, as it did not appear to be so well known, at least to chemists, as its importance to them, as well as to physiologists and biologists, would seem to deserve. In his book the author attacked, from a purely chemical point of view, the problem of the differences in character and properties of living as contrasted with dead protoplasm, and endeavoured to refer these differences to certain atomic rearrangements (which cannot be more minutely specified here) taking place within the albumin molecules of the protoplasm. Although he did not in any way commit himself to defending the author's views, the speaker strongly recommended the book to the attention of the members, as an interesting and eminently suggestive one.

CORRESPONDENCE.

CAMPHOR AND ITS DERIVATIVES.

To the Editor of the Chemical News.

Sir,—In a letter addressed to you by Prof. Noyes (Chem. News, vol. lxxvii., p. 70), your correspondent argues against one of two formulæ for camphor which he represents as introduced by me during a discussion at the Chemical Society.

May I remove an obvious misunderstanding on the part of Professor Noyes?

At the meeting in question a new formula for camphoric acid was employed by Drs. Crossley and Perkin. I pointed out that this would seem to necessitate the representation of camphor by one or other of two formulæ, of which one might be regarded as the more probable; but I added that "before either could be accepted, an explanation must be furnished of the changes involved in the production of such compounds as cymene and carvacrol from camphor—changes which, it must be remembered, are readily explained by Bredt's formula" (see Chemical News, vol. lxxvi., p. 297).

I do not prefer either of these formulæ to that of Bredt, which, in common with many chemists, I regard as the most satisfactory formula for camphor yet devised.—I am, &c.,

M. O. Forster.

The Royal College of Science, London, South Kensington, S.W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 4, January 24, 1898.

On an Interferential Spectroscope.—Ch. Fabry and A. Perot.—In a previous communication the authors have

referred to a new method of interferential spectroscopy; they now give more details of the arrangement of the apparatus. The method consists of observing the rings, localised to infinity, produced by the transmission through a film of air compressed between two plane surfaces of silvered glass. The two surfaces should be brought into perfect parallelism, and one of them must be fitted so that it can be moved away from the other, still retaining its parallel position, up to several centimetres. A sheet of glass silvered on each side may be used with excellent results, but in this case the thickness cannot be varied.

Conditions under which the Formation of the Alkaline Carbides, the Alkaline-earthy Carbides, and Carbide of Magnesium take place.—Henri Moissan.—This article will be inserted in full.

Separation of Thorium and the Cerite Earths.—G. Wyrouboff and A. Verneuil.—This paper will be inserted in full.

Hydramides and Isomeric Bases (Glyoxalidines).—Marcel Delépine.—The heat of formation of anisic aldehyd, $C_6H_4(CHO),(OCH_3)_4$, was found to be +63·1 cals.; that of anishydramine, $(C_8H_8O)_3N_2$, 48·4 cals.; that of anisine, $C_{24}H_{24}N_2O_3$, 64·6 cals.; that of furfuramide, $(C_5H_4O)_3N_2$, +0·35 cals.; that of furfurine, $C_{15}H_{12}N_2O_3$, 17·9 cals.; and that of chlorhydrate of furfurine, $C_{15}H_{12}N_2O_3,HCl$, +28·7 cals.

Researches on Ouabaine.—M. Arnaud.—The author has prepared a number of compounds and derivatives of this body which he hopes will help to define it from the chemical point of view. At least three different crystalline hydrates have been obtained by evaporating at temperatures of 10° to 20°, about 30°, and about 60°. The first contains 17·5 per cent of water when dried in the desiccator over sulphuric acid, the second 11·2 per cent, and the third 9 per cent. The rotatory power of ouabaine in a 1 per cent aqueous solution is $[\alpha]_D = -30·6°$.

Synthesis of Terebic Acid.—E. E. Blaise.—Terebic acid obtained by the method described at length by the author melts at 174°; its identification is made complete by its transformation into methyl-2-pentanolide, which is done by two consecutive slow distillations, and then warming for some minutes with sulphuric acid and water (2—1); this is neutralised with carbonate of soda and exhausted with ether. The alide thus produced boils at 206—207°.

Manufacture of Oil of Acetone, and especially Methylethylacetone, from the Wash-waters from Wool Cleaning.—A. and P. Buisine.—The volatile fatty acids isolated from these wash-waters are saturated with lime and the solution evaporated to dryness. The dried salts of lime are then distilled. The return of oil of acetone from waters of 11° Baumé is, by this method, about 15 litres per cubic metre, and the operation can be carried out at a very low price.

Anhydrous Sulphate of Lime produced by the Complete Dehydration of Gypsum.—A. Lacroix.—The object of this paper is to show that, by the complete dehydration of gypsum, a crystallised sulphate of lime is formed which is different to *anhydrite*. Crystals of gypsum were slowly heated in an oil-oven to 145°; they could then be polished as easily as before. Examination with polarised light shows that a dimorphous sulphate of lime is formed, probably triclinical in its crystalline form; both its refrangibility and its bi-refrangibility are much lower than those of anhydrite.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xvii.-xviii., No. 23.

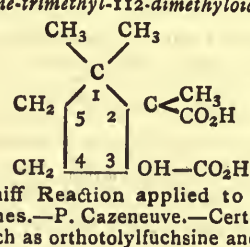
Remarks relative to the Note presented by R. Franchot entitled "On Nascent Hydrogen." — D. Tommasi.—The author asserts that M. Franchot has ignored his work on the subject of nascent hydrogen, carried out in 1877, and pulished in the *Comptes Rendus de l'Institut des Sciences de Milan*, 1877 and 1878.

On the Thermochemical Theory of a Battery with Carbon Electrodes. — D. Tommasi. — The author considers as inadmissible the theory that, in an electric battery with carbon electrodes such as his, the disengagement of electricity is entirely due to the chemical action of the chloride of sodium on the peroxide of lead surrounding one of the carbons—firstly, because in all voltaic couples in which the solution of chloride of sodium is used as the electrolyte, it is always the water that is decomposed, and never the chloride of sodium; and, secondly, because peroxide of lead has no action even on concentrated chloride of sodium.

Basic Salts of Magnesium. — M. Tassilly. — Oxychlorides of magnesium have long engaged the attention of chemists, though neither the oxybromide nor the oxyiodide had been prepared: the author has now succeeded in obtaining an oxybromide, though all his efforts to prepare an oxyiodide have been in vain. Three hundred grms. of water, containing 145 grms. of crystallised bromide of magnesium, were heated to boiling; the flame was withdrawn, and 5 grms. of calcined magnesia was added in small portions. It is again boiled, and the magnesia dissolves; towards the end of the operation the temperature is raised to 150°. The solution is filtered hot, and placed in a well-stoppered bottle. After a fortnight the oxybromide is deposited in small crystalline needles, acting on polarised light, showing longitudinal extinctions. The composition of this body answers to the formula $MgBr_2,3MgO,12H_2O$. When heated to 120° in dry air it loses half its water. These oxybromides undergo a change when exposed to the air, with the fixation of carbonic acid; they are decomposed by water, alcohol, and most reagents.

Syntheses by means of Tetrachloride of Phthalyl melting at 88°. Part I.—The Study of some Homologues of Diphenylanthrone.—A. Guyot.—A very long paper, not suitable for abstraction.

The Constitution of Camphoric Acid.—L. Bouveault.—Camphoric acid is bibasic, and has many points of resemblance with succinic and phthalic acids. It constitutes the *cyclo-pentane-trimethyl-1.1.2-dimethyloic-2.3*,—



On the Schiff Reaction applied to some Substituted Fuchsines.—P. Cazeneuve.—Certain homologues of fuchsine, such as orthotolylfuchsine and xylylfuchsine, are very sensitive to the action of aldehyds, after decolouration by SO_2. The colour obtained is bluer than with ordinary fuchsine.

The Congealing-point of Milk and some Allied Facts: Reply to Various Objections. — J. Winter.—This note is a *résumé* of a communication made by the author to the last meeting of the Society, in July, 1897, with the object of replying to several criticisms which had been passed on his work on this subject.

MISCELLANEOUS.

International Health Exposition.—This Exhibition will be held in the Industrial Building, New York, from April 25th to May 31st, 1898, under the supervision of Mr. Chas. F. Wingate. It will cover everything relating to health both in-doors and out-of-doors, and will show the progress made in sanitary matters during the century. An Educational Congress will also be held in connection

with the Exhibition, and a series of popular lectures will be provided every day during the time it is open. Exhibitors having appliances, or systems, which show a genuine advance, will be encouraged to provide lecturers or demonstrators themselves. The Exhibition will be divided into two principal departments, viz., Domestic Sanitation and Municipal Hygiene, these again being further subdivided into groups and sections.

MEETINGS FOR THE WEEK.

MONDAY, 21st.—Society of Arts, 8. (Cantor Lectures). "The Principles of Design in Form," by Hugh Stannus, F.R.I.B.A.

TUESDAY, 22nd.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LLD., F.R.S.

— Society of Arts, 8. "The Regalia of England," by Cyril Davenport.

WEDNESDAY, 23rd.—Society of Arts, 8. "Children's Sight," by R. Brudenell Carter, F.R.C.S.

THURSDAY, 24th.—Royal Institution, 3. "Some Italian Pictures at the National Gallery," by Jean Paul Richter.

FRIDAY, 25th.—Royal Institution, 9. "The Theory of Colour Vision applied to Modern Colour Photography," by Capt. Abney, C.B., D.C.L., F.R.S.

SATURDAY, 26th.—Royal Institution, 3. "The Structure of Instrumental Music" (with Musical Illustrations), by William H. Hadow, M.A., B.Mus.

— Physical, 4. (Instead of Friday, Feb. 25. In the Chemistry Lecture Room, Keate's Lane, Eton College). The Rev. T. C. Porter will describe:—1. A New Theory of Geysers. 2. A New Method of Viewing Newton's Rings. 3. Experiments bearing on the Sensation of Light. 4. A Method of Viewing Lantern Projections in Stereoscopic Relief. 5. Winter Observations on the Shadow of El Teide, with a New Method for Measuring approximately the Diameter of the Earth. 6. Temperature of the Water of Niagara.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 1996.

CONDITIONS UNDER WHICH THE FORMATION OF THE ALKALINE CARBIDES, THE ALKALINE-EARTHY CARBIDES, AND CARBIDE OF MAGNESIUM TAKE PLACE.

By M. HENRI MOISSAN.

By the aid of the electric furnace we have been able to prepare a large number of definite crystallised carbides, by reducing the oxides or carbonates by means of carbon. Certain of these, however, such as the alkaline carbides, cannot be prepared in this manner. It seemed interesting to find out why this method of preparation cannot be applied to this series of compounds.

In his paper, on a new class of metallic radicals, M. Berthelot (*Annales de Ch. et de Ph.*, Series 4, vol. ix., p. 385, 1886) announced the existence of the compounds C_2HNa and C_2Na_2, which were obtained by the action of a more or less elevated temperature on sodium, kept in an atmosphere of acetylene. The body C_2Na_2 thus formed is carbide of sodium, analogous by means of its collective properties to carbide of calcium, which I have prepared with ease in the electric furnace, and which has been the starting point of the acetylene industry. It seemed reasonable to imagine that the alkaline-earthy carbides, heated in an atmosphere of acetylene, might also form alkaline-earthy carbides. But the impossibility of obtaining these metals in a state of purity has prevented this experiment being carried out.

Carbide of Potassium.—M. Berthelot has prepared this compound by the action of acetylene at a dull red heat on the alkaline metal. When we heat a mixture of carbonate of potassium and carbon (CO_3K_2+2C) in the electric furnace, with a current of 900 ampères and 45 volts, we obtain a black pulverulent substance consisting of almost pure carbon, containing merely traces of the alkaline metal, and not producing any disengagement of gas on contact with water. Thus with a current of such intensity no carbide of potassium is formed. In a second experiment we heated the mixture of black flux and carbon, which is used for the preparation of potassium, in the electric furnace in a carbon tube closed at one end. The heating lasted eight minutes, and the current, weaker than before, was 45 volts and 350 ampères. After cooling, the product drawn from the tube was found to consist of a coarse powder, though some pieces had the appearance of mass, and of having been melted, thrown on water they immediately gave off gas. If this black substance be merely moistened with water it becomes incandescent, and gives off a gas burning with a reddish violet flame. Some fragments even produce a slight explosion. Treated with water in a tube filled with mercury it gives rise to a slight disengagement of gas. The black residue is formed of carbon, and the filtered water has taken a yellowish tint. This solution is very alkaline, and contains a small quantity of carbonate and of cyanide.

The gas given off consists of a little nitrogen, hydrogen, and acetylene. Two analyses of this gaseous mixture gave us 70 and 66·6 per cent of acetylene. The disengagement of gas is very slight, and the quantity of carbide of potassium produced under these conditions is very small. These first experiments show us that the temperature of the electric furnace is much too high to make the preparation of carbide of potassium possible by its use.

On the other hand, we have remarked that metallic potassium was slowly attacked in the cold at the ordinary pressure by acetylene gas. If the experiment is sufficiently prolonged the attack may even be complete. In one experiment we made, we placed a fragment of potassium in the top of a tube, 0·5 metre in length, closed at its upper extremity. This tube was filled with acetylene gas, and placed in a mercury bath. From the second day it was noticed that the level of the mercury was rising sensibly. The absorption continued slowly, and the experiment was stopped forty-nine days later.

At the commencement, the apparatus contained 17 c.c. of acetylene gas at 0° and 760 m.m. pressure; after the experiment the volume remaining was 8·35 c.c., containing 4·48 c.c. of hydrogen (the whole being reduced to 0° and 760 m.m). The volume of acetylene absorbed was 8·65 c.c. It is practically the double of that of the hydrogen produced, which may be explained by the following equation:—

$$\frac{C_2H_2}{2v} + K = C_2HK + \frac{H}{1v}.$$

We thus obtain in the cold a white product* adhering slightly to the tube, and which is decomposed by contact with cold water, giving pure acetylene. The volume of the gas obtained under these conditions was 7 c.c., which is slightly lower than the theoretical quantity. This slight difference is due to the polymerisation of a small portion of the acetylene. Thus in the cold, by the action of potassium on acetylene, we obtain the compound C_2HK, or potassic acetylene, already mentioned by M. Berthelot, an intermediary compound between acetylene C_2H_2 and carbide of potassium C_2K_2.

Carbide of Sodium.—The reduction of carbonate of sodium by carbon, under the influence of an intense current (1000 ampères and 70 volts), did not produce a carbide. On the contrary, by heating in a closed crucible, placed in a carbon tube, a mixture of soda and sugar-charcoal, by means of a weak current (350 ampères and 45 volts), we obtained a black powder, which, on contact with cold water, gave a slight disengagement of acetylene. The absorption of acetylene gas by sodium, in the cold, is much slower than with potassium; it is, in fact, almost *nil*.†

On account of this very slight absorption, we modified the experiment in the following manner:—A sealed tube was prepared containing sodium and dry liquid acetylene, and left at the temperature of the laboratory. At first the action is slow, but after several days the sodium becomes tarnished and covered with a layer of a yellowish white colour, the thickness of which keeps constantly increasing. At last the transformation of the metal is entirely complete. The tube, cooled down to a very low temperature, was at length opened, and the gas collected by means of a mercury pump. It was easy to separate the free hydrogen from the excess of acetylene.

The product, of a yellowish white colour, which has replaced the sodium, was analysed in the following manner:—A given weight of the compound was decomposed by water, and the acetylene collected and measured; it was then analysed to make certain of its purity. The sodium is estimated by the alkalimetric titration of the soda formed. The derivative thus obtained in the cold corresponds to the formula C_2HNa. This sodic acetylene, again, is the intermediate compound between acetylene and the carbide.

It is not indispensable to use liquid acetylene in this

* The transparent compound, which is produced by the action of potassium on acetylene in the cold, at first appears to possess a blue colour in the portions which were in contact with the metal when examined through a lens. This tint disappears as the transformation of the potassium takes place. This phenomenon may be compared with the blue colouration taken by chloride of potassium at a red heat in the presence of vapour of potassium, mentioned by Le Roux (*Comptes Rendus*, vol. lxvii., p. 1022, 1868), and which seems to result from the diffusion of the metal.

† The more easy formation of potassic acetylene explains why M. Berthelot met with traces of acetylene in the hydrogen produced by the decomposition of water on contact with potassium, while he found none in the hydrogen obtained by means of sodium.

operation; the same reaction can be carried out at the ordinary temperature with the compressed gas. The speed of the reaction, however, appears to be a function of the pressure. Thus, as we remarked above, the combination of sodium and acetylene is difficult to produce at the ordinary pressure, and it requires several months to become noticeable. At a pressure of one atmosphere the combination is more rapid, and if we heat slightly, even at a lower pressure, the attack proceeds with greater rapidity. Towards 50° it is already distinct, and we have succeeded in completely transforming a small fragment of sodium into the compound C_2HNa, by keeping it in contact with acetylene gas for fifteen days, at a temperature of 70°.

Dissociation of the Compound C_2HNa. — The white body having the formula C_2HNa, obtained by the action of acetylene upon sodium, in the cold, was placed in a tube of Bohemian glass closed at one end, and connected with a mercury pump. If this compound is slowly heated *in vacuo* we notice that it becomes brown, and at first gives off pure acetylene gas.

By continuing the heat the colour deepens, and, at the same time that the acetylene is given off, a small quantity of liquid carbides of hydrogen is condensed in the cold part of the tube. By then stopping the experiment, before spoiling the shape of the glass tube, the solid residue which remains gives off pure acetylene on contact with cold water: this is the carbide of sodium of M. Berthelot, having the formula C_2Na_2; if, instead of decomposing this compound with water, we continue to heat it *in vacuo* up to redness it will no longer give off any gas; black carbon only remains at the bottom of the tube,* and we notice a bright ring of metallic sodium condense above, in the cool part of the tube.

Thus, by elevating the temperature, *in vacuo*, to a point which need hardly reach the softening point of Bomemian glass, carbide of sodium is decomposed into carbon and sodium. This fact explains our want of success in our experiments on the reduction of soda, or of carbonate of sodium by carbon. The temperature of the electric furnace is much too high for carbide of sodium to be able to exist under these conditions. The preceding experiments may be represented by the two following equations:—

$$2C_2NaH = C_2H_2 + C_2Na_2$$
$$C_2Na_2 = C_2 + Na_2.$$

Carbide of Lithium. — We have already remarked, *à propos* of the preparation of carbide of lithium, that even with a current of 350 ampères and 50 volts, it is not necessary to heat for more than ten minutes, or else nothing but graphite remains at the bottom of the carbon tube in which the experiment was made. The temperature of this operation is of great importance from the point of view of the amount of carbide produced. This compound of lithium is in fact more easily dissociated by heat than is carbide of calcium. The temperature of decomposition of carbide of lithium is intermediate between that of carbide of sodium and that of the alkaline-earthy carbides.

Carbide of Calcium.—A certain number of experiments have shown us that, in the electric furnace, carbide of calcium can be decomposed if we make use of currents of too great intensity:—

1. In preparing small quantities of carbide of calcium with currents of 1200 ampères and 60 volts, it has happened, if the experiment lasts ten minutes, that we have obtained a residue of pulverulent graphite, containing only traces of carbide of calcium. The compound has not volatilised, for the carbon remains in the crucible. It is more reasonable to suppose that a dissociation of the carbide has taken place, the calcium distilling off with ease, leaving the pulverulent residue of carbon.

2. In the experiments made by means of a cold Deville tube, which were carried out with the object of studying the condensation of the vapour of carbon, we never obtained any condensation of carbide of calcium. If, in fact, we heat melted carbide of calcium in the electric furnace, all we find on the copper tube, through which cold water is kept circulating, is graphitic dust, pulverulent lime, and calcium; this latter, on contact with water, gives off hydrogen, the purity of which has been verified by a eudiometric analysis. As with the carbides of sodium and lithium, but at a much higher temperature, carbide of calcium can be decomposed into the metal, and carbon.

Carbide of Magnesium.—By carefuly heating powdered magnesium in a current of acetylene gas (a reaction suggested by M. Berthelot), we obtain an impure carbide of magnesium, mixed with carbon, but unmistakably giving acetylene gas on contact with cold water.

This carbide of magnesium was placed in a double crucible of pure graphite, and heated in a carbon tube closed at one end, using 600 ampères and 60 volts; the experiment lasted six minutes. After cooling, the black material taken from the bottom of the crucible gave no disengagement of gas on contact with water. The carbide of magnesium was totally decomposed under the influence of this high temperature. This experiment perhaps explains why we have been able to melt magnesia and bring it to quite a liquid state in carbon crucibles, without this oxide being in any way reduced. At the temperature of fused magnesia, carbide of magnesium can no longer exist.

Conclusions.—To sum up, by the action of cold acetylene gas, or by the action of liquid acetylene, with or without pressure, we can obtain the intermediate sodic and potassic acetylenes in a state of purity, C_2KH and C_2NaH. By elevating the temperature these bodies can be decomposed; they cause a disengagement of acetylene, and they leave as residue the carbides C_2K_2 and C_2Na_2.

By a much greater elevation of temperature these carbides are dissociated into the metals and carbon. The phenomenon is identical with the carbides of the alkaline earths, though a much higher temperature is required. The same holds good with carbide of magnesium.

The stability of these carbides, under greater and greater variations of temperature, goes on increasing from the alkaline metals up to the alkaline-earthy metals.

These experiments have established the fact that the carbides of potassium, sodium, and of magnesium cannot be produced at the temperature of the electric furnace.—*Comptes Rendus*, cxxvl., No. 4.

* We have shown, by experiment, that this powder was formed of ure carbon. t no longer gave off any gas on contact with water. ...

SOME REMARKS ON THE PRODUCTION OF STEEL CASTINGS.

By SERGIUS KERN, M.E., St. Petersburg.

In 1894 we introduced the crucible steel process for the production of steel castings at the New Admiralty, St. Petersburg. The coke steel furnace gives daily nearly 3 cwts. of steel; this quantity is the production of four crucibles per heat. An annealing furnace is attached to the small foundry; every casting being subjected to the annealing process in charcoal.

The moulding sand consists of about 90 per cent of fine quartz sand and 10 per cent of the best fire-clay. This mixture is mixed with a small quantity of sawdust and rye-flour. As a wash for mouldings, malt boiled with water is used.

We consider that ferro-silico-manganese is the most powerful agent as an addition to ready-made steel for the production of sound castings; the most useful alloy containing, on the average, 10 per cent of silicon and 15 per cent of manganese. Metallic aluminium is of second importance, especially if good raw materials are used; we prefer an addition of ferro-aluminium (14 per cent of aluminium) with the silico-manganese.

For steel castings the following raw materials are used:—Roundings coming from the punching of soft steel ship-plates for rivet holes, and soft puddled iron. The plates contain on the average 0·4 per cent of manganese, and such material is suitable—as we remarked that steel castings containing some 0·6 per cent of manganese, even if annealed, are somewhat dry and of a crumbling nature.

Once a month the chemical composition of steel castings is ascertained. In the ordinary run, the composition of various castings for ship-building is as follows:—

Carbon	0·40 per cent.
Manganese	0·42 ,,
Silicon	0·35 ,,
Sulphur	0·02 ,,
Phosphorus	0·04 ,,

The mechanical tests on pieces half an inch in diameter and four inches in length give:—21 tons per square inch as elastic limit, 45 tons per square inch as resistance, with an elongation of 8 to 10 per cent.

In case of castings to resist water or steam pressure, we prefer the use of steel stronger in carbon, and have 0·6 per cent of carbon in the metal. Such a metal we recommend for the different pieces of Belleville boilers, mostly hollow and of capricious forms.

The crucible charge for ordinary castings contains:—

Steel plate roundings	50 pounds.
Steel plate shearings	10 ,,
Puddled iron	20 ,,

When the charge is melted, which results after some five hours, an addition is made, consisting of—

Silico-manganese	0·75 of a pound.
Ferro-aluminium	0·15 ,, ,,
Ferro-manganese (containing 80 per cent Mn)	0·10 ,, ,,

In total, the addition weighs 1 pound, and is introduced into each crucible by means of a funnel, and remains there for twenty minutes. After this lapse of time the crucibles are taken out, and the casting commenced. Some minutes after, the moulds are opened, the castings released, and covered again with the moulding sand. In such a state they cool, being finally introduced into the annealing furnace.

The crucible charge for water-tight castings consists of—

Ship-plate roundings	55 pounds.
Ship-plate shearings	10 ,,
Puddled iron	12 ,,
Refined best cast-iron	3 ,,

The following is the addition for such a steel:—

Silico-manganese	0·70 of a pound.
Ferro-aluminium	0·25 ,,
Ferro-manganese (containing 80 per cent Mn)	0·15 ,,

This addition, before the casting, remains in the crucible for twenty-five minutes.

The refined cast-iron used in the charge is very pure, coming from charcoal blast-furnaces; and after refining, which is done by re-melting the material in crucibles, contains:—

Total carbon	3·78 per cent.
Manganese	0·58 ,,
Silicon	0·28 ,,
Phosphorus } Sulphur }	0·03 ,,

There is a good field here for private works of steel castings. The big establishments make castings for their own use only—having no time for outside orders,—and the one or two small steel foundries work still empirically, sending out good and bad material. We had in hand steel castings sent to the Admiralty and rejected; they contained 0·75 per cent of carbon.

February 14, 1898.

ON CHEMICALLY INACTIVE ELEMENTS.

By Dr. JOACHIM SPERBER.

Inasmuch as the elements, with the exception of hydrogen as unity, act with a force or valency which is not in proportion to their atomic weights, I drew the following conclusions, based on the doctrine of the parallelogram of forces:—

1. That atoms enter into reaction at definite angles in such a manner that the valency only indicates the value of the component which the atom contributes, in the direction of the molecular movement in the resulting compound.

2. That the valency of an element (V) equals the atomic weight (a) into the cosine of the angle (ϕ), at which the atom enters into combination.

$$V = a \cos. \phi.^*$$

This angle will in some instances depend on the direction of the vibrations of the atom itself within the molecule; in other instances, in the direction of the vibration of the molecule itself. For—

$$\phi = 90^\circ$$
$$\cos. \phi = 0$$
$$V = a.0 = 0;$$

that is, if an atom vibrates at right angles to the molecular vibrations—as, for instance, in the case of an atom with transverse vibrations in the presence of gases with their strong tendency to longitudinal vibrations—it has no valency, therefore no affinity, and consequently cannot enter into chemical combination.

My theory of valency, therefore, presumes the existence of elements that cannot enter into chemical combination, because their atoms have a prevailing tendency to transverse vibrations; there is, too, substantial proof of this, for the cosmic ether is without doubt such an element, since, as is known, it does not enter into chemical combination, and its vibrations are transversal. Moreover, the chemically inactive elements, argon and helium, have recently been discovered; and if they cannot be made to enter into chemical combination,—as up to the present is the case, in spite of zealous endeavours in that direction,—then, in accordance with my theory of valency, this is to be attributed to a prevailing tendency on the part of their atoms to vibrate transversally, which brings these elements into close relationship to the cosmic ether, perhaps to be regarded as condensation products of different grades.

It is important to confirm this, for when once the cause of the inactivity of argon and helium is known, the sooner will a means be discovered for rendering them active.

We know from experience that atoms of elements have less affinity among themselves than towards other atoms; the greater activity of nascent elements is, indeed, due to this fact. When, therefore, the atoms of an element show no affinity towards other atoms, they can have no affinity among themselves. Hence it follows that the inactive elements must be monatomic; this likewise agrees with all we know up to the present about argon and helium.

International Photographic Exhibition at the Crystal Palace, 1898.—H.R.H. The Prince of Wales has graciously consented to open the Exhibition. Intending exhibitors are asked to note that the date of opening of the Exhibition by His Royal Highness has been fixed by him for Monday, April 25th, and not Wednesday, April 27th, as originally announced. The latest date for the reception of exhibits in each Section will therefore be two days earlier than that first stated on the prospectus.

* This presumes components at right-angles, as are spontaneously and frequently engendered in Nature.

THE KEKULÉ MEMORIAL.

The death of August Kekulé on February 13, 1897, terminated a career rich in scientific achievement. In him we have lost an investigator who has exerted a profound influence on the development of chemistry.

The theory of valency and of the linking of atoms, and our present views as to the structure of carbon compounds, have acquired their definite form and clearness by the labours of Kekulé. His theory of benzene derivatives in particular has given the most powerful impulse to investigation in the domain of pure chemistry; while no scientific theory has done more to promote the development of chemistry as a branch of industry.

While Kekulé is eminent by his scientific achievements, he is not less so by reason of the effects produced by his teaching. The publication of his "Lehrbuch der Organischen Chemie" marked an epoch in the history of chemistry. This treatise has done more to familiarise chemists with modern views than any other work of the kind.

The greater number of German professors of chemistry, and many of those in other countries, have either studied under Kekulé or under those who were his pupils; and gratitude calls for some permanent memorial of his striking personality.

Such a memorial would be a statue in bronze of the founder of structural chemistry, which would be fitly placed in front of the Chemical Institute at Bonn—in the place where, for thirty years, he lived, and taught, and worked.

All friends, admirers, and pupils of Kekulé are accordingly invited to contribute to this object. Subscriptions will be forwarded to the Central Committee at Bonn, and will be received by Dr. Hugo Müller, 13, Park Square East, Regent's Park, N.W.

James Dewar,
G. Carey Foster,
T. E. Thorpe,
Hugo Müller,
Francis R. Japp,
Raphael Meldola.

ON THE DISSOCIATION SPECTRA OF MELTED SALTS.

SULPHUR, PHOSPHORUS, AND THE SOLID PHOSPHOROUS COMPOUNDS.

By A. de Gramont.

Sulphur.

Salts containing sulphur, sulphides or sulphates, when submitted to the action of the condenser spark in the apparatus I have previously described, give a very brilliant spectrum of the sulphur lines, the same as with solid metallic sulphides (mineral conductors, for instance), and free sulphur, either melted and solidified on two electrodes in the air, or contained in a Salet tube. The melted salts, however, have this advantage over minerals, that they can be freed from foreign matters which would complicate the spectrum, especially in the violet (principally iron and calcium lines). For the purpose of this investigation, I chose the alkaline sulphates in preference to the sulphides; the latter attacking to a certain extent the platinum wires and spatulas on which they are melted. If, in the dissociation spectra obtained, lines of considerable brilliancy are always present, the appearance of faint and hardly visible lines would seem to depend on the quality of the spark or on the resistance to dissociation of the compound under examination; and if, by corresponding variations of these two factors, we are enabled to obtain a complete line spectrum, we must not, on the other hand, be astonished at the absence of some of the fainter lines at any particular moment, under known conditions. I will now give a complete list of the lines of sulphur compounds produced by the condenser discharge either with free sulphur, melted salts, or with minerals. The measurements, made with a spectroscope with two prisms, have been corrected to the normal spectrum of Rowland. The Greek letters denoting the principal group are those used by Salet; I have only added ϕ and ψ for two groups of red lines easily seen in all sulphur compounds.

	657·6	Fairly well seen.
	645·4	Faint.
S ϕ	641·65	,,
	640·25	Well marked.
	639·0	,,
S ψ	632·0	Fairly strong.
	630·95	,,
	629·1	,,
	615·35	Faint; doubtful.
	601·65	Very faint; doubtful.
	586·7	Fairly well seen.
	581·75	Very faint.
S α	567·3	Fairly strong.
	566·3	Strong.
	565·2	,,
	564·3	,,
	562·3	Fairly well seen.
	560·85	Strong.
	558·4	Faint.
	556·95	,,
	555·95	,,
	552·85	,,
	551·45	,,
	550·85	Well marked.
S β	547·35	Fairly strong.
	545·3	Strong.
	543·5	,,
	543·0	Fairly strong.
S γ	534·35	Strong.
	532·1	,,
	522·8	Well seen, but doubtful.
S δ	521·95	Fairly strong.
	521·3	Strong.
	520·2	,,
	516·1	Fairly well seen.
	514·35	Well marked.
	512·85	Faint.
	511·4	,,
	510·3	Well marked.
	504·6	Well seen.
S ε	503·7	,,
	503·25	Strong.
	502·2	Fairly strong.
	501·45	Well seen; diffuse.
	499·55	Fairly strong.
	494·2	Faint.
S ζ	492·55	Fairly strong.
	490·5	Fairly well seen; diffuse.
	488·5	Faint; vague.
	482·7	Hardly visible.
S η	481·5	Fairly strong.
	480·5	Faint.
	479·4	,,
	478·2	,,
	476·6	Hardly visible.
	475·7	,,
S θ	471·65	Fairly strong.
	466·6	Hardly visible.
	465·5	,,
	463·3	Fairly well seen.
	461·6	Faint; doubtful.
	456·2	Faint; diffuse.
S μ	455·2	Strong.
	452·6	,,
	448·5	,,
	446·45	,,

	442·85	Faint; diffuse.
	438·8	,, ,,
	435·0	,, ,,
	434·2	Hardly visible; doubtful.
	433·6	Faint; doubtful.
	432·8	,, ,,
S π	429·55	Strong.
	428·4	,,
	427·9	Faint.
	426·95	Fairly strong.
	425·95	Faint.
	425·15	Fairly strong.
	424·15	Faint.
	422·55	,,
S ρ	417 (about)	Faint; diffuse.
	416 ,,	,, ,,
	415 ,,	,, ,,

I would here point out that I am not certain as to the sulphur lines that I have described as *doubtful*.

S ψ, formed of bright lines, is easily seen in all compounds of sulphur. S α, of which the strong lines are very close to the Group β of air, is very characteristic, but difficult to determine when arsenic and lead are also present, which frequently happens in the case of minerals. S β, S γ, S δ are the brightest and most characteristic groups in this spectrum, and are very distinct even with only one prism; the intercalation of the metallic lines hardly weakens them, with the exception of those of copper and lead in the case of S δ. But S γ appears to be the most persistent and most sensitive group of the spectrum. In spite of the brightness of its lines, S ε is not of much use in analysis, for it is mixed with the important Group α of air, from which it is very difficult to free it, even when the spark occurs in the body of the melted salt in the flame itself. The three blue lines S ζ, S η, S θ, relatively less strong in melted salts than in free sulphur, are, however, easy to recognise. The groups S μ and S π are, on the contrary, often difficult to distinguish in sulphur compounds, where the condensation necessary to dissociate these latter blurrs them so much that they can hardly be distinguished. I have, in the table, given the intensity of these lines in free sulphur. S ρ is only visible with a good deal of light and a non-absorbent apparatus. I have not been absolutely certain of it in any compounds.

To sum up, the groups which should be used for the identification of sulphur are:—Firstly, S β, S γ, S δ, in the green; and, secondly, S φ, in the red; S α, S ε, in the green, and S ζ, S η, S θ in the blue. I would, finally, remark that the lines have appeared to me to be more sharp, distinct, and less enlarged when using sulphates than sulphides. This difference, however, has not seemed to me to be sufficiently decisive to be perfectly characteristic.

Phosphorus.

The spectrum of phosphorus is one of the easiest to obtain by the dissociation of melted salts; the condensation obtained by one Leyden jar being sufficient to show it. The line spectrum thus produced is far better, both in sharpness and intensity, than that obtained by the use of Plücker or Salet tubes, which have, as in the case of sulphur, been exclusively used up to the present.

In this work I have principally used alkaline phosphates, and I now give the measurements of the wave-lengths of the phosphorus lines corrected to the normal spectrum of Rowland. The alphabetical descriptions of the lines are those used by Salet in his "Traité de Spectroscopie." The lines marked * were not observed by him.

	650·7	Easily seen; diffuse.
	645·9	Well marked.
	608·9	Easily seen.
P α	604·3	Very strong; bright.
	603·55	Fairly strong; bright.
	602·6	Very strong; bright.
P β	549·95	Fairly well seen.
	546·3	Faint.
	545·4	,,
P γ	542·45	Very strong.
	* 541·0	Strong.
	* 538·6	,,
	* 534·1	Strong; rather diffuse.
	531·2	,,
	529·3	,,
P δ	525·1	Very strong.
	* 496·9	Fairly well marked; diffuse.
	494·2	Well marked.
P ε	460·4	Very strong.
	458·95	,,

The difference in intensity between the lines marked *very strong* and those marked *strong* is not very great. The most characteristic and sensitive groups are:—First, the triple red P α and the double blue P ε, both of which are easily recognised at first sight; and, secondly, the series of green lines from P γ to P δ. Those which were not recorded by M. Salet correspond in intensity, and approximately in position, with the lines given by Plücker in the plate attached to his memoir, and from which Mr. Watts has deduced (approximately) their wave-lengths.

The Solid Phosphorous Compounds.

The solid phosphorous compounds, when subjected to the condenser spark, give at once in the cold a line spectrum of phosphorus as beautiful as that obtained from melted phosphates. A slight condensation is sufficient even for bodies which are non-conducting but volatilisable in the spark. The proportions between the relative intensities of the lines are the same as with the melted salts, which, as above, will furnish comparative spectra. By this means we can easily detect the phosphorus lines in metallurgical products, even when they are mixed with the metallic lines.

The phosphides of copper, for example, give a particularly brilliant spectrum of phosphorus, because of the small number of metallic lines present. Among the different phosphorous alloys, the large number of iron lines would appear at first sight to make the detection of phosphorus a difficult matter. It is, however, easily recognised by the characteristic triple orange line P α (604·3, 603·5, 602·6), whose brightness is almost equal to that of the iron lines, which are notably weak in this region. This reaction takes place perfectly plainly in alloys containing only 2 per cent of phosphorus, but it is not very distinct in the case of alloys containing smaller quantities; it becomes less and less certain until, at about one-thousandth, the lines are practically invisible. In the same manner, a metallic phosphide, insoluble in acids, isolated by M. Friedel from the Cañon el Diablo meteorite, gave me the principal phosphorus lines in the midst of those of iron and nickel.

Sulphophosphides or Thiohypophosphates.—As an example of the spectral examination of non-conducting solid bodies—which are, however, volatilisable in the electric spark—I will take the new series of sulphophosphides discovered by M. Friedel (*Comptes Rendus*, vol. cxix., 1894), and obtained by him in the crystalline form in sealed tubes at a high temperature; they correspond to the formulæ $P_2S_6M_{4\,I.}$ or $P_2S_6M_{2\,II.}$. Through the kindness of M. Friedel, I was enabled to observe that their direct spark spectra are the same as those of the corresponding natural minerals, metallic sulphides, already described, but that they further show the phosphorus lines much more strongly and much brighter than those of sulphur, in spite of the fact that the percentage proportion present of this body is about three times as great as that of the phosphorus in this series of sulphophosphides. A condenser surface equal to a small Leyden jar of 5 or 6 square decimetres is sufficient to cause the spectrum of phosphorus to appear most distinctly, while it is necessary to use two or three jars (about 25 to 35 square decimetres) to obtain

that of sulphur—the intensity of which, under these conditions, never appears to be so great as with the corresponding minerals. Thus, with $P_2S_6Fe_2$ the sulphur lines are more brilliant and more easily seen than in pyrites; while with $P_2S_6Cu_4$ they are less bright than in chalcosine. $P_2S_6Ag_4$ is comparable with argyrose; $P_2S_6Pb_2$, with galena; and $P_2S_6Hg_2$, with cinnabar. All three of these are better conductors than the compounds of tin, $P_2S_6Sn_2$ and P_2S_6Sn, which require three jars to give a good spectrum of sulphur, and are by no means comparable with any corresponding mineral.

These examples will suffice to show the ease and simplicity of the direct spectral analysis of solid compounds, even when bad conductors. A little practice will enable one, by making slight variations in the arrangement of the apparatus, to apply this method to widely different substances.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 2.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 10th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us, all were found to be clear, bright, and well filtered.

There has been a serious deficiency in the rainfall during the month of January, rain having fallen on five days only, viz., the 4th, 5th, 6th, 16th, and 31st, and then to only a small extent; the actual figures are:—Rainfall at Oxford, 0·82 inches; thirty years' average, 2·16 inches; deficiency, 1·34 inches.

Our bacteriological examinations of 251 samples have given the results recorded in the following table; we have also examined 40 other samples, from special wells, standpipes, &c., making a total of 291 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	2377
New River, filtered (mean of 26 samples) ..	19
Thames, unfiltered (mean of 26 samples) ..	4263
Thames water, from the clear water wells of five Thames-derived supplies (mean of 123 samples)	52
Ditto ditto .. .. highest	386
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	2866
River Lea, from the East London Company's clear water well (mean of 24 samples) . ..	25

For the time of year, the rivers Thames and Lea are in exceptionally good condition, owing to the lack of rain, but at the same time it is satisfactory to see from the above results that the filtering plant of the various companies is in good working order, and that with the exception of one or two abnormally high results, which after all did not include pathogenic organisms, the bacterial quality of the water supplied to London is excellent.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

SALTS OF DINITRO-ALPHA-NAPHTHOL WITH VARIOUS METALLIC BASES.*

By T. H. NORTON and H. LOWENSTEIN.

THE preparation and study of the following compounds were undertaken with the view of ascertaining whether in addition to the few salts of dinitro-α-naphthol thus far known, there might not be other combinations with metallic bases possessing a greater degree of solubility than the commercial calcium salt (Manchester yellow, Martius Gelb) now so largely used, or more especially showing distinct variations in the colour imparted to animal and vegetable fibres. The results showed that in the latter respect the metal present is practically without influence on the tinctorial properties of dinitro-α-naphthol, the tint yielded in each individual case being essentially that imparted by the free phenol or by its calcium salt.

The salts of dinitro-α-naphthol thus far examined and analysed are those with sodium, potassium (Hübner, *Ann. Chem.* (Liebig), ccviii., 332), ammonium, barium, strontium (Martius, *Journ. Prakt. Chem.*, cii., 443), calcium (Darmstädter and Wichelhaus, *Ann. Chem.* (Liebig), clvii., 201; Liebermann, *Ann. Chem.* (Liebig), clxxxiii., 249; Martius, *vide supra*), and silver (Hübner, *Ann. Chem.* (Liebig), ccviii., 332).

The dinitro-α-naphthol used was prepared by precipitating the concentrated aqueous solution of the commercial calcium salt by dilute sulphuric acid, washing the precipitate thoroughly with water, drying, and extracting the liberated phenol by boiling alcohol. The finely crystallised product thus obtained possessed the melting-point of 138°.

Lithium Dinitro-α-naphtholate, $C_{10}H_5(NO_2)_2OLi$.

This salt is obtained in solution by boiling an excess of dinitro-α-naphthol with an aqueous solution of lithium carbonate and filtering. On evaporation it is deposited in the form of a brilliant crimson powder, which is amorphous and anhydrous. The salt, on being heated to 295°, explodes before melting. It is soluble in 96 parts of water at 19°, in 14 parts of boiling water, in 50 parts of cold alcohol, in 15 parts of boiling alcohol, and in 300 parts of ether. It is insoluble in carbon disulphide and in benzene. The temperature of solutions, unless otherwise noted, is 18° C.

The salt, dried between sheets of bibulous paper, lost no weight on heating to 105°. The analyses were made by adding concentrated sulphuric acid to weighed amounts in a platinum crucible, evaporating to dryness, and ignition as lithium sulphate. Care is necessary to avoid spattering.

I. 0·246 grm. of the dry salt gave 0·0535 grm. lithium sulphate, equal to 0·0069 grm. of lithium, or 2·80 per cent.

II. 0·256 grm. gave 0·0535 grm. lithium sulphate, equal to 0·0068 grm. of lithium, or 2·88 per cent.

* Contributions from the Chemical Laboratory of the University of Cincinnati. From the *Journal of the American Chemical Society*, xix., No. 12.

	Calculated for $C_{10}H_5N_2O_8Li$.	Found. I.	II.
Lithium	2·87	2·80	2·88

Magnesium Dinitro-α-naphtholate, $[C_{10}H_5(NO_2)_2O]_2Mg$.

This salt is prepared by boiling in water a mixture of magnesium carbonate with an excess of the naphthol. It crystallises slowly from the filtered solution in the form of reddish needles, grouped in rosettes. It is anhydrous, the salt dried between sheets of bibulous paper, losing no weight when heated to 105°. It is soluble in 792 parts of water at 20°, in 154 parts of boiling water, in 436 parts of cold alcohol, in 144 parts of boiling alcohol, and in 260 parts of ether. It is insoluble in benzene and carbon disulphide.

The first three analyses were made by igniting the substance in a platinum crucible, in which a smaller inverted crucible was wedged, so as to prevent as much as possible mechanical loss by explosive decomposition, and weighed as magnesia.

In the fourth analysis the substance was strongly heated in a sealed tube. After cooling, the tube was opened, its contents were dissolved in dilute nitric acid, and the solution was evaporated to dryness, ignited, and weighed likewise as magnesia.

I. 0·035 grm. of the salt dried at 105° gave 0·0025 grm. magnesium oxide, equal to 0·0015 grm. magnesium, or 4·28 per cent.

II. 0·1557 grm. gave 0·0113 grm. magnesium oxide, equal to 0·067 grm. magnesium, or 4·35 per cent.

III. 0·1552 grm. gave 0·012 grm. magnesium oxide, equal to 0·0072 grm. magnesium, or 4·64 per cent.

IV. 0·0623 grm. gave 0·0039 grm. magnesium oxide, equal to 0·0023 grm. magnesium, or 3·77 per cent.

	Calculated for $(C_{10}H_5N_2O_8)_2Mg$.	Found. I.	II.	III.	IV.
Magnesium . ..	4·87	4·28	4·35	4·64	4·77

Zinc Dinitro-α-naphtholate, $[C_{10}H_5(NO_2)_2O]Zn$.

This is obtained by boiling together in water an excess of the naphthol with zinc carbonate. From a hot concentrated solution it crystallises out in the form of handsome reddish yellow needles, while more dilute solutions yield reddish crystals, possessing the shape of rhomboidal plates. In this respect the zinc salt resembles the calcium salt (Liebermann, *Ann. Chem.* (Liebig), clxxxiii., 249).

It is soluble in 960 parts of water at 20°, in 300 parts of boiling water, in 250 parts of cold alcohol, in 115 parts of boiling alcohol, and in 150 parts of ether. It is insoluble in benzene and carbon disulphide. The salt is anhydrous; crystals dried between sheets of bibulous paper losing no weight at 105°.

The explosive nature of the compound renders necessary in analysis the careful use of the two crucibles described above, small amounts being taken. Even with these precautions a small loss is unavoidable.

I. 0·123 grm. of the salt dried at 105° gave 0·017 grm. zinc oxide, equal to 0·0136 grm. zinc, or 11·09 per cent.

II. 0·108 grm. gave 0·016 grm. zinc oxide, equal to 0·0128 grm. zinc, or 11·89 per cent.

	Calculated for $(C_{10}H_5N_2O_8)_2Zn$.	Found. I.	II.
Zinc	12·22	11·09	11·89

Copper Dinitro-α-naphtholate, $[C_{10}H_5(NO_2)_2O]Cu$.

This salt is obtained by adding an excess of a concentrated solution of copper chloride to a cold aqueous solution of ammonium dinitro-α-naphthol. The chocolate coloured precipitate is washed with water until all traces of copper chloride are removed, and dried between sheets of bibulous paper. Thus prepared, it is an anhydrous dark brown amorphous powder, the most insoluble of the salts of the naphthol thus far known.

It dissolves in 5750 parts of water at 21°, in 2165 parts of boiling-water, in 1007 parts of cold alcohol, in 954 parts of boiling alcohol, and in 2615 parts of ether. It is insoluble in benzene and carbon disulphide.

The analyses were performed by gently heating the salt with concentrated nitric acid in a covered porcelain crucible, and finally igniting. As in the preceding cases, the explosive nature of the salt renders the utmost care necesary.

I. 0·2663 grm. of the salt dried at 105° gave 0·036 grm. cupric oxide, equal to 0·0287 grm. copper, or 10·79 per cent.

II. 0·1665 grm. gave 0·023 grm. cupric oxide, equal to 0·0183 grm. copper, or 11·03 per cent.

III. 0·3033 grm. gave 0·0443 grm. cupric oxide, equal to 0·0353 grm. copper, or 11·67 per cent.

	Calculated for $(C_{10}H_5N_2O_8)_2Cu$.	Found. I.	II.	III.
Copper ..	11·97	10·79	11·03	11·67

Solubilities of the Ammonium and Calcium Salts.

No data existing on the solubilities of these two compounds, the following determinations were made:—

Ammonium dinitro-α-naphtholate is soluble in 600 parts of water at 25°, in 38 parts of boiling water, in 113 parts of cold alcohol, in 57 parts of boiling alcohol, and in 1124 parts of ether.

Anhydrous calcium dinitro-α-naphtholate is soluble in 1656 parts of water at 20°, in 86 parts of boiling water, in 47 parts of cold alcohol, in 15 parts of hot alcohol, and in 45 parts of ether.

THE RELATION OF THE TASTE OF ACIDS TO THEIR DEGREE OF DISSOCIATION.

By THEODORE WILLIAM RICHARDS.

Since no systematic attempt appears to have been made to determine acids quantitatively by means of the sense of taste alone, it seemed worth while to carry out the following series of experiments with this idea in view.† The peculiar sourness which is distinctive of acids is probably to be referred to the hydrogen ion, which also is distinctive of them, and it becomes a question of no small interest to determine how closely the taste corresponds to the degree of dissociation.

The sense in question is well known to be rather an uncertain one, depending upon the habits and physical condition of its possessor, so that an experimenter could hardly expect to obtain absolute results from its use. On the other hand, relative taste, determined by alternately tasting two solutions, might well furnish some clue as to the relative strength of these solutions.

The water used in the experiments recorded below was distilled in a platinum still over alkaline permanganate, the first portions of the distillate being rejected. For the final experiments this water was re-distilled; in this way an unusually tasteless liquid may be obtained. The solutions of acids, alkalies, and salts were carefully made of pure materials. The test was accomplished by simply taking a small mouthful (5 c.c.) of the liquid in question (which is advantageously warmed beforehand to 40°), and allowing this liquid to remain upon the tongue for a few seconds until a constant intensity of taste is secured. A

† Contributions from the Chemical Laboratory of Harvard College. From the *American Chemical Journal*, vol. xx., No. 2.

† Dr. Squibb has used this physiological method upon cocaine with good results. ("Ephemeris of Materia Medica, &c.," Brooklyn, N.Y., vol. iii., No. 1, p. 918, 1887). My attention was called to this interesting work after the present paper was written, and I know of no similar investigation.

few of the individual experiments are recorded below in order to define the method, but most of them are merely indicated in the conclusions.

(1) To four several portions of water, each measuring 10 c.c., were added respectively 0·05, 0·10, 0·20, and 0·30 c.c. of decinormal hydrochloric acid. The first of these solutions remained unchanged in taste, the second became faintly acid, and the others very distinctly so.

(2) In order to test the degree of accuracy attainable in this way, a number of beakers containing dilute acid were "shuffled," so that the identity of each was lost, and the attempt was then made to arrange them according to strength by means of the taste alone. Small inconspicuous labels showed finally how successful the attempt had been. In the first trial, four beakers, each containing 30 c.c. of water, were acidified by adding 0·2, 0·4, 0·6, and 0·8 c.c. of decinormal hydrochloric acid. These were arranged by taste without great deliberation in their proper order, showing that the method is capable of an accuracy of 25 per cent, even with a comparatively unpractised tongue.

(3) Another similar trial was made with similar amounts of water containing 0·3, 0·4, 0·5, and 0·6 c.c. of decinormal acid respectively. After repeated tasting and much deliberation these were arranged in the order 1, 2, 4, 3; thus my success with the method did not go beyond 20 per cent, although the limit might unquestionably be reduced by practice.

Similar experiments with sulphuric, nitric, and hydrobromic acids showed that the sensitiveness in these cases is about the same—an acid of the concentration of somewhat less than $\frac{1}{100}$ normal, representing the limit of possible detection as indicated by my sense of taste. This is a very weak solution, containing less than a milligrm. of hydrogen ions in a litre.

It is, of course, possible that a part of this taste might be due to the negative ion. Further light upon this point is obviously to be obtained by neutralising the acid with potash or soda. It was found in this way that an acid liquid which tasted distinctly sour became absolutely tasteless upon neutralisation; indeed, a centinormal solution of potassium chloride has less taste than a millinormal solution of acid. According to the dissociation hypothesis, the hydrogen ions have been removed by the neutralisation, and we are now tasting potassium and chlorine ions, which are either not very strong in taste, or else have the peculiar property of nearly eliminating one another's taste by mixture. Since most properties of solutions are additive, and we cannot well conceive of a *minus* taste (except such a subtraction from the taste as might be caused by a partial paralysis of the nerves, owing to some very powerful excitement), the former alternative seems to be the most natural one; hence we may believe that neither potassium nor chlorine ions possess as strong a taste as those of hydrogen.

It becomes now a matter of interest to compare these results with those given by very dilute solutions of less ionised acids. Tartaric acid thus diluted, tasted somewhat less sour than a corresponding solution of the mineral acids, citric acid was still less sour, and acetic acid was the least sour of all. While qualitatively these observations agree with those which we should expect to make, the quantitative agreement is less satisfactory. Acetic acid, for instance, seemed to taste at least as strong as hydrochloric acid of one-third its concentration, whereas at a concentration of $\frac{1}{512}$ normal, Kohlrausch's experiments upon its electrolytic conductivity show that only about one-fourteenth of the acid is dissociated.* The reason for this discrepancy is not evident, unless the act of tasting removes the dissociated part of the acid, and so leaves room for further dissociation, or unless the undissociated acid possesses a taste resembling that of the hydrogen ions, but weaker. Both of these hypotheses carry one too far into physiological chemistry to receive treatment here.

Somewhat more satisfactory were the results of mass action upon the taste. The addition of small amounts of potassic chloride to very dilute solutions of hydrochloric acid produced no appreciable effect upon the taste, while the sourness of acetic acid was noticeably diminished, and that of hydrochloric acid was almost destroyed by adding similar amounts of potassic or sodic acetates. These phenomena are qualitatively in accord with the dissociation hypothesis and the mass law, which tell us that in such a reaction as

$$CH_3COOH \rightleftarrows H+ + CH_3COO-$$

the addition of a large proportion of acetic ions from the almost wholly dissociated sodic acetate is capable of forcing the reaction backwards and destroying the hydrogen ions. The case is, of course, analogous to the effect of salts in modifying the catalytic action of acids upon cane-sugar and esters, as measured by Ostwald (*Journ. Prakt. Chem.*, 1883, 28, 449; also 1885, 31, 307), Arrhenius (*Zeit. Physikal. Chem.*, 4, 226), Spohr (*Journ. Prakt. Chem.*, 1885, 32, 32), Trevor (*Zeit. Physikal. Chem.*, 10, 321), Palmaer (*Ibid.*, 22, 492), and others. We should expect, however, to find the taste of the acetic acid wholly destroyed by the addition of sodic acetate, because the acid's power of inverting sugar is so much diminished thereby; and the fact that some acid taste remains is only to be accounted for by some such hypothesis as those given above. The fact that the taste of hydrochloric acid is diminished much more than that of acetic acid by the addition of sodic acetate is not inconsistent with these hypotheses; for acetic acid, whether wholly or partly undissociated, has been shown to be much less sour than hydrochloric acid; and acetic acid is undoubtedly formed in this case.

A common application of these principles is to be found in the preparation of the much-used "soda water" or "mineral water" of commerce. Unless a small amount of sodic carbonate is added during its preparation, the effervescent solution is so sour as to be unpleasant to some tastes. This sourness may sometimes have been augmented by a stronger acid carried over in the process of careless preparation; but the fact that it exists in some degree, even in carefully prepared carbonic acid water, was shown by experiment in the laboratory. In any case the sourness is removed by sodic bicarbonate, and the hypothetical explanation is similar to that given above. The following equilibrium is usually assumed to exist in the solution of carbonic acid:—

$$H_2CO_3 \rightleftarrows H+ + HCO_3-.$$

The acid is, however, only very slightly dissociated. Hydric sodic carbonate, on the other hand, is probably largely dissociated into Na+ and HCO_3-, and when this salt is added these latter ions force back the already very slight dissociation of the carbonic acid, rendering the solution pleasant and soft to the taste by removing some of the hydrogen ions.

Since sodic chloride was found to possess a taste so much feebler than that of hydrochloric acid, it is evident that the sense of taste might form a fairly sensitive indicator of the end-point of an acidimetric reaction. It is possible easily to detect sourness in a millinormal solution of acid, hence in working with decinormal solutions of acids and alkalies we ought to be able to determine the end-point to within 1 or 2 per cent.

Accordingly several titrations were made with exactly decinormal solutions of hydrochloric acid and sodic hydroxide, the liquid being tasted with a glass rod until the end-point was nearly reached, when small mouthfuls were tasted. The alkalinity of saliva is insufficient to make any essential difference in the results. If large amounts of liquid are removed, it is obviously necessary to allow for the acid or alkali thus taken out; but this

* At 18°, when $v=167$ $\mu=17{\cdot}0$; $v=500$ $\mu=28{\cdot}3$; $v=\infty$ $\mu=318{\cdot}4$ } *Wied. Ann.*, 26, 161, 1885.

correction may be reduced to a very small amount by the use of large quantities of the original solutions.

The best results were obtained by adding slightly too much acid, and then adding alkali until the sour taste just disappeared. The figures are given below—the first and second columns containing the number of cubic centimetres of acid and alkali respectively, and the third the percentage of acid found.

Acidimetric Titration.

C.c. of acid taken.	C.c. of alkali taken.	Per cent of acid found.
7·00	6·99	99·9
10·73	10·67	99·4
7·21	7·15	99·1
14·96	14·99	100·2
14·44	14·59	100·9
	Average	99·9

The accuracy of these results, which were obtained in an unprejudiced fashion, is somewhat astounding. Evidently, in the course of the few experiments described here, the sense of taste had been noticeably sharpened. To what limit this sensitiveness might be carried it is hard to predict; but already the method of analysis had assumed a degree of accuracy exceeding some which are seriously applied as quantitatively useful.

Efforts were made also to analyse the taste produced by weak currents of electricity, as well as the effect of sugars in mitigating the unpleasantness of great acidity of taste, but the complex physiological relations involved in these and similar cases led to an unsatisfactory outcome.

The results of this paper, although they are only qualitatively consistent with the theory of dissociation, nevertheless show that the sense of taste might be used more precisely in the laboratory than is usually believed.

THE ELECTROLYTIC DETERMINATION OF CADMIUM.*

By DANIEL L. WALLACE and EDGAR F. SMITH.

About a year ago Max Heidenreich (*Ber. d. Chem. Ges.*, xxix., 1585) published an article in which he reviewed methods proposed by one of us (S.) for the electrolytic determination of certain metals. In some instances he confirmed the observations of Smith, but in most cases differed with him. Recently S. Avery and Benton Dales (*Journ. Amer. Chem. Soc.*, xix., 380) announced that so far as the determination of cadmium was concerned their "result was in complete harmony with the experiments of Heidenreich." In consequence of these experiences with the electrolytic methods suggested by Smith for the determination of cadmium, we have repeated them, and offer new results obtained by us.

It was in 1878 (*Proc. Am. Phil. Soc.*, Nov., 1878) that Smith stated that "0·1450 grm. of cadmium oxide was dissolved in acetic acid, the excess of the latter expelled upon a water-bath, and the platinum crucible then about half filled with water, and . . . connected with the negative pole of a two-cell Bunsen battery. . . . The deposition of the cadmium was regular . . . a perfectly crystalline, greyish white layer." The precipitation was complete in about three hours. The experiment was repeated, but a bichromate battery was substituted for the Bunsen cells. At the time when these trials were made, current strength in definite units was not given: hence subsequent workers have met with difficulty in repeating some of the early work, and perhaps that may account for the failure to precipitate cadmium from the solution of its acetate. We have sought to obtain the original working conditions given by Smith, have stated them in definite units, and append results obtained by their observance.

Experiment 1.—0·1329 grm. of cadmium oxide was dissolved in acetic acid, the solution was evaporated to dryness, and the residue dissolved in 30 c.c. of water. The liquid was then heated to 50° C., and electrolysed with a current of 0·02 ampère for 37 sq. c.m. of cathode surface. Voltage 3·5. The metal was completely precipitated in four hours. It was crystalline and perfectly adherent. There was no evidence of sponginess. The hot acid liquid was syphoned off, and replaced by water without interrupting the current. We found that the period of precipitation could be diminished, and very good results be obtained by adding 1 grm. of ammonium acetate to the solution when the current had acted for an hour. The quantity of metallic cadmium present in this particular experiment was 0·1162 grm., while that actually found equalled 0·1158 grm.

Experiment 2.—0·1332 grm. of oxide, treated precisely as outlined in Experiment 1, gave 0·1164 grm. of adherent crystalline metal instead of 0·1165 grm.

With these results before us we see no cause why the deposition of this metal from its acetate solution should be condemned. Neumann ("Theorie und Praxis der Analyt. Elektrolyse," p. 129) mentions it as being possible, and Yver (*Bull. Soc. Chim.*, xxxiv., 18) even used an acetate solution in the electrolytic separation of cadmium from zinc.

Smith (*Am. Chem. J.*, ii., 41) published experiments made by him on the precipitation of cadmium from solutions containing free sulphuric acid. As this method seems not to have proved satisfactory in the hands of Heidenreich, and of Avery and Dales, we have repeated the work, and offer the following experiments as evidence in favour of the Smith method.

Experiment 1.—0·1270 grm. of cadmium oxide was dissolved in 2 c.c. of sulphuric acid, sp. gr. 1·09, and the solution then made up with water to 30 c.c. It was heated to 50° C., and electrolysed for a period of 4½ hours with a current of 0·08 ampère for 37 sq. c.m. cathode surface. Voltage 2·5. The deposit weighed 0·1105 grm. instead of 0·1111 grm. It was crystalline and adherent. Tendency to sponginess was not observed. The acid liquid was syphoned off before interrupting the current. The filtrate showed no signs of cadmium when tests were made for it.

Experiment 2.—In this trial 0·1358 grm. of cadmium oxide was dissolved and treated as in Experiment 1. The deposit of metal weighed 0·1181 grm. instead of 0·1188 grm.

We have never experienced any difficulty in the application of this method, and are also pleased to observe that Neumann (*loc. cit.*) gives an example confirming the early recommendation of Smith. It is this: "die Lösung von 0·3 grm. Kadmium sulfat in 150 c.c. Wasser mit 1 bis 2 c.c. verdünnter Schwefelsäure versetzt, wird auf 70 bis 80 Grad C., erwärmt und bei diesem Temperatur durch Ströme von 0·6 bis 1 ampère zersetzt. Die Spannung schwankt . . . zwischen 2·5 bis 5 volt . . . Der Niederschlag ist silberweiss."

Our experiences with the precipitation of cadmium from a phosphoric acid solution will be reserved for a subsequent communication.

We regard the double cyanide solution (*Ber. d. Chem. Ges.*, xxv., 779) as the best adapted for the deposition of cadmium. Further evidences of this are the many atomic weight determinations made of this metal, in which this particular solution was employed (*Ztschr. Anorg. Chem.*, i., 364; *Journ. Amer. Chem. Soc.*, xviii., 1022).

The first suggestion for the electrolytic separation of copper from cadmium was also made by Smith (*Am. Chem. J.*, ii., 43). He demonstrated that, in the presence of free nitric acid, copper was deposited in satisfactory form, while the cadmium continued in solution.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xix., p. 870.

Heidenreich (*loc. cit.*), in speaking of this method, which has received frequent confirmation, remarks: "eine Reihe von Versuchen, Kupfer von Kadmium aus einer freie Saltpetersäure enthaltenden Lösung zu trennen, führten zu keinem befriedigenden Ergebnisse." In reply to this we offer the following experiments:—

Experiment 1.—To a solution containing 0·3893 grm. of copper sulphate (= 0·0988 grm. of copper) and 0·1152 grm. of cadmium oxide (= 0·0985 grm. of cadmium) were added 2 c.c. of nitric acid, sp. gr. 1·43. The total dilution of the solution equalled 100 c.c. It was heated to 50° C., and electrolysed with a current $N.D._{100} = 0·10$ ampère. Voltage 2·5. The metal was completely precipitated in three hours. It was bright in colour, and satisfactory in every respect. It weighed 0·0988 grm. and did not contain cadmium.

Experiment 2.—A solution containing the same quantity of copper and 0·1203 grm. of cadmium oxide, when treated exactly as in Experiment 1, gave 0·0987 grm. of copper. It was free from cadmium.

To these results we would add the observation of Neumann ("Electrolyse," p. 169): "Am einfachsten is zur trennung von Kupfer und Kadmium immer die Verbindung der mil *freier Saltpetersäure* versetzten Lösung beider Salze."

Heidenreich maintains that the separation of copper from cadmium succeeds "sicherer aus einer mit *Schwefelsäure* versetzten Lösung." This solution had been previously recommended by Smith (see "Electrochemical Analysis," 2nd ed., p. 108), and his observations were confirmed by Freudenberg (*Ztschr. Phys. Chem.*, xii., 97).

The results recorded in the preceding paragraphs justify us in saying that cadmium can be successfully determined electrolytically when working either with its acetate or sulphate, and that its separation from copper in the presence of nitric acid is in every respect satisfactory.

The failure of Heidenreich to precipitate uranic oxide by means of the current will be considered later.

TESTING OF FORMALDEHYD.*

By CARL E. SMITH.

THE rapidly increasing uses of formaldehyd make it desirable that standards be established for the strength and purity of the commercial products. A method of assay, simple and rapid, as well as reasonably accurate, is needed as a guide for manufacturer and pharmacist, as also tests for the various impurities liable to be present, and reactions to establish its identity. As the commercial solutions vary considerably in quality, ready means should be at hand for controlling the quality of the pharmacist's supply.

Assay Methods.

A method of assay, to be generally applicable, must not be affected in accuracy by the presence of ordinary impurities frequently contained in commercial formaldehyd solution, such as methyl alcohol and acetone; neither should it require much time and attention or complicated operations. Of the number of methods which have been published within recent years, the principal ones were examined, in order to ascertain which of them approaches nearest to these requirements, with the results stated below:—

Hydroxylamine Method.—Proposed by Brochet and Cambier (*Compt. Rend.*, vol. 120, p. 449, and *Ztsch. f. Anal. Chem.*, vol. 34, p. 623). Based on the reaction of hydroxylamine hydrochloride and formaldehyd, with the liberation of hydrochloric acid, according to the following equation:—

$$NH_2OH.HCl + H.COH = CH_2N(OH) + HCl + H_2O.$$

The formaldehyd entered into combination is determined by the amount of acid set free.

In the experiments made the details prescribed by the authors were followed, except that N/10 soda solution was used for titrating the hydrochloric acid instead of N/10 borax solution.

Ten c.c. of a solution containing 0·0864 grm. of a concentrated formaldehyd solution were mixed in a small flask, with 10 c.c. of a 2·5 per cent solution of hydroxylamine hydrochloride. (The hydroxylamine salt is about five times the amount involved in the reaction. This large excess was afterwards found unnecessary, 50 per cent excess being quite sufficient). After standing ten minutes the liberated acid was titrated, requiring, after deducting 0·1 c.c. for free acid in the hydroxylamine solution, 10·7 c.c. of N/10 soda; 1 c.c. = 0·003 grm. formaldehyd.

$$\frac{10·7 \times 0·003 \times 100}{0·0864} = 37·2 \text{ per cent.}$$

Several trials were made to determine the time limit of the reaction.

Allowing twenty minutes to complete the reaction, the result was 37·2 per cent.

Allowing forty-five minutes to complete the reaction, the result was 37·3 per cent.

Other trials showed that shaking the mixture does not materially hasten the reaction, and that it is practically complete in seven to eight minutes after admixture.

The above figures agree closely with those obtained on the same solution by other methods.

The method is quick and accurate, when applied to pure solutions, but the accuracy is interfered with by the presence of other aldehyds and acetone, as stated by G. Romijn (*Ztsch. f. Anal. Chem.*, vol. 36, p. 18). For acetone the statement was verified by a simple test-tube experiment; aldehyds were not tried.

Iodine Method.—Proposed by Romijn (*ibid.*). Nearly identical with Messenger's process for estimating acetone, and therefore unsuitable for the assay of solutions liable to contain *acetone*. It was used only to determine the strength of pure solutions, made from para-formaldehyd, and for this purpose was found accurate and convenient. A very dilute solution of the formaldehyd is mixed with an excess of N/10 iodine solution, and caustic alkali solution added until the iodine is decolourised. After standing ten minutes dilute acid is added to liberate the excess of iodine, and this estimated with sodium hyposulphite.

Cyanide Method.—Also devised by Romijn (*ibid.*). It is based upon the formation of an addition product of formaldehyd and potassium cyanide, from which the cyanide cannot be precipitated with silver nitrate. It involves the use of standard solutions of silver nitrate, potassium cyanide, and potassium sulphocyanate. This method requires much more care and attention than any of the others tried, and a few trials showed conclusively that it is not likely to give satisfactory results except in practiced hands. It was, therefore, considered useless to proceed further with it.

Fixed-Alkali Method.—This consists in heating the formaldehyd with sodium or potassium hydrate solution under pressure, in a manner similar to that in the saponification of esters. The formaldehyd is converted into methyl alcohol and formic acid as follows:—

$$2CH_2O + KOH = CH_3OH + KCHO_2.$$

The method was most satisfactory when conducted as follows:—Three grms. of the sample are placed into a strong bottle of 50 c.c. capacity, with 25 c.c. of N/1 soda solution, the bottle closed with a tight-fitting rubber stopper, this tied down with a cord, and the bottle, after

* Report of Research Committee DII., Committee of Revision of the United States Pharmacopœia. From the *American Journal of Pharmacy*, lxx., No. 2.

wrapping with a cloth, immersed in boiling water for one-half hour. After cooling, the excess of soda is titrated with N/1 sulphuric acid and phenolphthalein, each c.c. of soda solution consumed indicating 0·06 grm., or, if 3 grms. be taken, 0·5 per cent of formaldehyd.

The time required to complete the reaction is very much less than is stated by others who have tried the method, nor were some other stated disadvantages noticed, such as thickening or resinifying of the solutions. The results were reasonably accurate, except in the case of one commercial sample. The following figures illustrate the duration and degree of heat necessary. They were all obtained with the same formaldehyd solution :—

Heated *in* boiling water.	Per cent.	Heated *over* boiling water.	Per cent.
15 minutes	37·1	15 minutes	32·5
30 „	37·3	30 „	34·5
1 hour	37·6	1 hour	37·1
2 hours	37·2	2 hours	37·7
		3 „	37·3

On *prolonged* heating the solution frequently darkens so as to make dilution necessary before titrating.

The influence of the presence of acetone and methyl alcohol on the accuracy of the methods was determined.

(To be continued).

NOTICES OF BOOKS.

Bibliography of the Metals of the Platinum Group. Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium, 1748—1896. By Jas. Lewis Howe. Smithsonian Miscellaneous Collections, No. 1084. City of Washington: published by the Smithsonian Institution. 1897. 318 pp., 8vo.

By the industry and ability of Professor Jas. Lewis Howe, M.D., Ph.D., of Washington, and Lee University, in Virginia, and through the liberality of the Smithsonian Institution, chemists are furnished with another invaluable work of reference, having the above title.

The well-printed volume contains about 2300 references to original papers, and probably nearly twice as many references to reproductions and abstracts of the same. These references are preceded by a list of the one hundred periodicals examined, and are followed by two exhaustive indices—a classified subject-index and an alphabetical author-index.

This bibliography forms one of a series compiled under the auspices of the Committee on Indexing Chemical Literature of the American Association for the Advancement of Science, and will prove indispensable to chemists working on the metals named. H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 5, January 31, 1898.

M. Cremona was elected a correspondent for the Geometrical Section, in succession to the late M. Brioschi.

Composition of Air in different Places, and the Density of the Gases.—A. Leduc.—The air in Paris contains 232 parts by weight of oxygen per 1000; in Havre, 230·5; at sea, 232·1; at Nice and Algiers, 232·3; while that in London contains only 231 parts. The densities of oxygen, atmospheric nitrogen (which is a mixture), pure nitrogen, carbonic oxide, and carbonic acid are given, both in comparison with air and with oxygen. They agree very closely with Lord Rayleigh's results.

Decomposition of Hyposulphite and Sulphite of Strontium by Heat, and the Production of Phosphorescent Strontic Sulphide.—J. R. Mourelo.—When hyposulphite of strontium is decomposed by heat a mixture of sulphate of strontium, sulphide of strontium, and sulphur is always formed, of which the relative quantities produced depend on the temperature reached and the time of the operation. When the heating is properly regulated, it is not difficult to obtain a complete decomposition according to the equation—

$$4S_2O_2Sr = SSr + 4S + 3(SO_4Sr).$$

It possesses the maximum yellowish green phosphorescence when it contains 15·02 parts of sulphide of strontium, 16·12 parts of sulphur, and 68·45 parts of sulphate of strontium. The success of the operation depends on arresting the oxidation at a definite point. If sulphite of strontium is heated under the same conditions it is transformed entirely into sulphate of strontium; but, as before, by properly regulating the temperature, the phosphorescent mixture is obtained according to the formula $4SO_3Sr = 3(SO_4Sr) + SSr$, the best proportion is found to be 14·05 parts of sulphide of strontium and 85·94 parts of sulphate of strontium.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xvii.-xviii., No. 24.

M. Desgrez announced that, even in the cold, chloroform decomposes when in contact with a weak solution of potash, giving no longer formic acid, but carbonic oxide and water; chloral and bromoform give the same reaction; but iodoform, methyl-, and phenyl-chloroform do not give off any gas. The author feels sure that this formation of carbonic oxide in an aqueous alkaline solution could be profitably used in the toxicological search for chloroform.

M. Muttelet, by causing the para-nitrated derivative of chloride of benzoyle to react on the mono-substituted ortho-diamines and on the nitrated derivatives of the ortho-diamines, has obtained nitro-amidines, which are isomers of the nitro-amidines already described by him (*Bull. Soc. Chim.*, xvii., p. 865).

MM. Labbé and Flatau made a communication on some new crystalline compounds, by means of which they are enabled to distinguish, with certainty, geraniol and citronnellol.

While studying the different combinations which occur in steel on the addition of various elements, such as P, As, Si, Cr, Mn, M. Carnot has been able to isolate a certain number of definite compounds by attacking the steels, either with dilute acids or with chloride of copper.

M. Delépine has observed that when aldehydate of ammonia is dried *in vacuo* over sulphuric acid, it loses the elements of water and gives ethylidene-imine, hitherto unknown.

On the Preparation and Properties of the Borides of Calcium, Strontium, and Barium.—H. Moissan and P. William.—Already noticed in this column.

Application of the Friedel and Crafts Method to the Preparation of Acetones and Aromatic Aldehyds.—L. Bouveault.—A controversial paper concerning one recently published by M. Verley.

On the Nature of the Combination of Antipyrine with the Aldehyds.—G. Patein.—The author has endeavoured to establish, firstly, whether antipyrine really gives two kinds of compounds with formic aldehyd in particular and the aldehyds in general; and, secondly, if chloral is also capable of giving two kinds of compounds, and he finds that the aldehyds combine with antipyrine in the proportion of *one* molecule of aldehyd to *two* mole-

cules of antipyrine: this manner of combination is the only one, and the union is always made by means of the carbon, and never by the nitrogen. This does not apply to the chlorine derivatives, and chloral can only unite with antipyrine by means of the nitrogen.

The Action of Chloride of Benzoyle-*p*-nitrated on the Mono-substituted Ortho-diamines.—F. Muttelet.—The author describes the action of chloride of benzoyle-*p*-nitrated in excess, and hot, on the following ortho-diamines:—*o*-amido-phenyl-aniline, *o*-amido-phenyl-*p*-toluidine, *p*-nitro-*o*-amido-phenyl-aniline, and *p*-nitro-*o*-amido-phenyl-*p*-toluidine, and also the properties of each of these new nitro-amidines.

The Saccharines.—P. Monnet and J. Koetschet.—A reply to the paper recently published by M. Sisley (p. 84, 1897), in which he claims priority for the preparation of colouring matters derived from saccharine, described by the authors in the same publication (p. 690, 1897).

MISCELLANEOUS.

The Manchester Steam-Users' Association has recently issued a large printed sheet, suitable for display in boiler-houses, headed "Advice to Boiler Attendants," wherein will be found precise instructions as to the proper working of, and attending to steam-boilers, both with regard to water-level, lighting fires, smoke prevention, emptying boilers, overhauling, cleaning and inspecting, &c. Also a list of "Warnings" as to possible accidents and their causes; also what to do and what not to do in such cases: it is naïvely remarked that the boiler attendant may prefer to retire at such a time; he should certainly not expose himself unnecessarily in front of the furnaces, but should warn others of the danger.

Royal Institution.—On Thursday next (March 3rd) Professor J. A. Fleming, F.R.S., will deliver the first of a course of five lectures at the Royal Institution, on "Recent Researches in Magnetism and Diamagnetism"; and on Saturday (March 5th) Professor Walter Raleigh will begin a course of three lectures on "English Letter Writers." The Friday Evening Discourses this week (Feb. 25th) will be delivered by Captain Abney, C.B., F.R.S., whose subject will be "The Theory of Colour Vision applied to Modern Colour Photography." On March 4th Professor T. E. Thorpe, F.R.S., will deliver the Discourse; his subject is "Some Recent Results of Physico-chemical Inquiry."

MEETINGS FOR THE WEEK.

Monday, 28th.—Society of Arts, 8. (Cantor Lectures). "The Principles of Design in Form," by Hugh Stannus, F.R.I.B.A.

Tuesday, March 1st.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.

Wednesday, 2nd.—Society of Arts, 8. "Kites—their Theory and Practice," by Captain B. F. S. Baden-Powell.

Thursday, 3rd.—Chemical, 8. "Note on the Preparation of Dry Hydrogen Cyanide and Carbon Monoxide," by J. Wade, B.Sc., and L. C. Panting, M.B. "Production of some Nitro- and Amido oxylutidines," by J. N. Collie, Ph.D., F.R.S., and T. Tickle. "Production of some Nitro- and Amido-oxylutidines" (Part II.), by J. N. Collie, Ph.D., F.R.S., and Miss L. Hall. "The Interaction of Magnesium and Solution of Copper Sulphate," by E. Divers, M.D., F.R.S.

—— Royal Institution, 3. "Recent Researches in Magnetism and Diamagnetism," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.

Friday, 4th.—Royal Institution, 9. "Some Recent Results of Physico-Chemical Inquiry," by Professor T. E. Thorpe, LL.D., D.Sc., F.R.S.

Saturday, 5th.—Royal Institution, 3. "English Letter Writers," by Professor Walter Raleigh, M.A.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 1997.

ON FEHLING'S SOLUTION.

By OTTO ROSENHEIM, Ph.D., F.C.S., and PHILIP SCHIDROWITZ, Ph.D., F.C.S.

In a recent communication under the above heading (Chemical News, vol. lxxvi., p. 318) we showed that the alkali salts of mineral acids have no influence on the reducing power of Fehling's solution. We were led to investigate the matter in consequence of a paper by M. Z. Jovitschitsch (*Ber. Deutsch. Chem. Ges.*, xxx., 2431), in which it was asserted that Fehling's solution is reduced by mineral acids when the reaction of the solution is still distinctly alkaline.

From the perusal of Jovitschitsch's paper, we—and we should imagine any other reader (see also J. E. Gerock, *Apoth. Ztg.*, xii., 800; and *Ber. Deutsch. Chem. Ges.*, xxx., 2865)—were forced to the conclusion that the reduction is due to the action of mineral acids (*in an alkaline solution!*) on tartaric acid; more especially as Jovitschitsch's very words are "that the acids mentioned" [*in an alkaline solution* (authors)] "favour the decomposition of the tartaric acid; in fact, the tartaric acid itself . . . . causes reduction."

We refrained from discussing the matter fully in our first note, for reasons then mentioned, and because we considered the figures published therein sufficiently convincing. But as M. Siegfried (on whose observation Jovitschitsch's paper was based) has lately published a note (*Ber. Deutsch. Chem. Ges.*, xxx., 3133), according to which the (supposed) reduction is now ascribed by him—there was no mention of this in Jovitschitsch's paper—to the deficient alkalinity of the solution caused by the addition of the mineral acids in question, we feel induced to publish the remainder of our qualitative and quantitative experiments.

According to Jovitschitsch's somewhat vague statement—which, by the way, has already formed the subject of abstracts in various journals (see *Journ. Soc. Chem. Ind.*, xxvi., 1046; *Journ. Chem. Soc.* 73 and 74, 1898)—the reduction is best carried out as follows:—

"One or two drops of the mineral acid—not too strong (?)—are added to 1—2 c.c. of strongly (?) alkaline Fehling's solution; that is, till the latter is still somewhat blue or slightly alkaline. Then a few drops of the original Fehling's solution are added. A turbidity similar to that formed by grape-sugar, phenylhydrazin, &c., is immediately produced, and on gently warming the solution the reduction thus commenced is completed." (N.B.—We translate literally).

We have made numerous experiments in strict accordance with Jovitschitsch's instructions, but not in a single instance—even after prolonged boiling—did we observe the slightest reduction (*cf.* also J. E. Gerock, *loc. cit.*; *Centralbl. Zuckerindustrie*, vi., 245). Quantitative experiments with 25 c.c. of freshly-prepared Fehling's solution and HCl, H_2SO_4, HNO_3 respectively, also gave negative results. In each case the solution was boiled for one minute.

In another series of experiments a constant volume of the solution was first acidified by the addition of hydrochloric, sulphuric, nitric, and tartaric acids respectively in slight excess, and then fresh Fehling's solution added till the reaction was distinctly alkaline to litmus. In every instance the solution remained perfectly clear in the cold.* On boiling, however, a slight turbidity, which was not increased by four minutes' continuous ebullition, was formed. This turbidity was caused by a small quantity of a yellow substance suspended in the liquid. After filtering through a Soxhlet's asbestos tube, the solution was observed to be of the same colour as before, and did not produce any further turbidity on renewed boiling for some minutes. It was evident from the figures obtained before and after oxidation that the yellow substance only consists in part of hydrated cuprous oxide, and contains varying percentages of organic matter (*cf.* Ed. Nihoul, *Chem. Zeit.*, xvii., 500; xviii., 881). The carbonic acid formed by the combustion of the organic matter in a current of oxygen was identified by passing the gases into baryta. It will be seen from the figures below that the quantity of reduced copper (after heating in oxygen and subsequently in hydrogen) is so small that it is practically negligible*; it is apparently constant and independent of the quantity of solution used.

Jovitschitsch fears that the reduction mentioned above may have been a frequent source of error in the qualitative examination of liquids with Fehling's solution, but we consider this is out of the question. When using *pure* Fehling's solution, the turbidity formed is so slight that it could hardly deceive the veriest novice. It is, of course, clear that we do not wish to recommend the omission of the traditional rule that all liquids to be examined with Fehling's solution must first be made alkaline.

The following were the figures obtained by boiling 25, 50, 100, and 200 c.c. respectively, after adding acids, as described above:—

Acid used.	25 c.c. Fehling's solution. Weight of precipitate.		50 c.c. Fehling's solution. Weight of precipitate.	
	Before oxidation and reduction.	*After* oxidation and reduction.	*Before* oxidation and reduction.	*After* oxidation and reduction.
		Grm. Cu.		Grm. Cu.
Tartaric acid ..	0·0022	0·0007	0·0027	0·0009
Sulphuric acid .	—	0·0002	0·0022	0·0006
Nitric acid ..	0·0020	0·0010	0·0016	0·0002
Hydrochloric acid	—	0·0010	0·0020	0·0002
	100 c.c. Fehling's sol.		200 c.c. Fehling's sol.	
Sulphuric acid .	0·0017	0·0006	0·0025	0·0009

* M. Siegfried (*loc. cit.*) has modified Jovitschitsch's original communication by stating that reduction does not take place till the liquid is boiled.

* It is even smaller than the quantity obtained by boiling dilute Fehling's solution with or without the addition of alkali salts (*cf.* Chem. News, vol. lxxvi., 318).

ON THE SEPARATION OF THORIUM, AND THE EARTHS OF CERITE.

By G. WYROUBOFF and A. VERNEUIL.

After having found a method for the separation of cerium from lanthanum and didymium, and the whole of the earths of the yttria group, we sought for a more convenient and more certain method than those yet known for getting rid of the thorina. In all the reactions made use of for the separation of the cerite earths, thorium remains partly, if not entirely, with the cerium. This occurs particularly in the method of separation which we have already described. If only a few hundredths are present, they are completely precipitated at the same time as the cerosoceric nitrate.

If we require simply to obtain pure cerium, we dissolve the precipitate in a sufficient quantity of hydrochloric acid to reduce the cerium to the state of protoxide, add a little phosphoric acid to the warm solution, and evaporate to a pasty consistency; then take up with water, and

filter. All the thorina remains in the insoluble state, retaining a few hundredths of cerium. The filtered liquid contains protochloride of cerium, perfectly free from thorium.

The inverse problem—the preparation of thorina perfectly free from cerium—is much more difficult, and, as is well known, it can only be achieved after a long series of operations, without which we can obtain no precise characteristic, except the absence of incandescence, for the purpose of recognising its purity.

Some time ago (*Bull. Soc. Chim.*, xliii., p. 57, 1885) M. Clève announced a curious reaction, which belongs only to thorina among the rare earths: on adding peroxide of hydrogen to a solution of sulphate of thorium we obtain a gelatinous precipitate which has for formula—

$$Th_4O_7,SO_3 (Th = 116).$$

By studying this reaction more closely we observed that by using the nitrate as exempt from the free acid as possible, and adding an excess of H_2O_2 and heating to about 60°, we precipitate the whole of the thorium present in the solution. The reaction is so sensitive that we can not only detect one part of thorium in a thousand of either cerium or of the mixed earths of cerite and gadolinite, but we can even collect and weigh it. It is true that the thorina thus precipitated still contains some cerium, especially if this latter is present in great excess. But by re-dissolving this impure thorina in nitric acid, evaporating to dryness, and precipitating once more with H_2O_2, we can obtain a thorina containing not more than 0·1 per cent of impurities. A third precipitation removes these last traces of cerium, and after a fourth precipitation the filtered liquid does not give the slightest precipitation with ammonia. In practice, and especially if working on several hundred grms. of material, it is better to commence by treating the mixture of nitrates with an excess of a 10 per cent solution of carbonate of ammonia to which a little caustic ammonia has been added. All the thorina thus passes into solution, carrying only a few hundredths of the other earths with it. A single precipitation with peroxide of hydrogen then suffices to obtain a precipitate of thorina almost perfectly pure, and giving only a trace of incandescence.

It remained for us to apply this simple and rapid method to the quantitative estimation of thorium in the presence of the other rare earths; but here altogether unexpected difficulties were met with. The nitrate of the peroxide, $Th_4O_7N_2O_5$, cannot be calcined, as in losing its oxygen it decrepitates, and is reduced to a powder of such extreme tenuity that it is thrown right out of the crucible, which may easily lead to a loss of 10 per cent. On the other hand, it is impossible to dissolve it on the filter, in either nitric or hydrochloric acid, so as to transform it into hydroxide, the calcination of which is easy; in fact, such a considerable disengagement of oxygen takes place that, whatever precautions one takes, a certain quantity of the solution is carried off in imperceptible drops. After a large number of attempts we decided on the following method, which, as will be seen further on, gives perfectly satisfactory results. The solution of the nitrates, which should not contain more than 0·5 of oxides, is evaporated to dryness, and taken up with 100 c.c. of water and 10 c.c. of peroxide of hydrogen,* and heated for some minutes while stirring. The extremely voluminous precipitate is thrown on a filter and washed until the wash water no longer gives a precipitate with ammonia. The precipitate is detached from the filter,—an operation which is not at all difficult, owing to the gelatinous nature of the peroxide,—and dissolved in a few c.c. of water, containing 2 grms. of NH_4I and 2 c.c. of concentrated HCl; the reduction is instantaneous. The hot solution is run through the filter to dissolve the proportions of the precipitate still adhering to it, then washed. The solution is precipitated by ammonia; the hydroxide, which does not need washing, is thrown on the same filter and calcined. In the filtered liquid of the peroxide, all the other earths which accompany thorium are precipitated by ammonia. The precipitate obtained by means of peroxide of hydrogen ought to be perfectly white. If such is not the case—which happens whenever cerium is present in any considerable quantity—it is necessary to re-dissolve the hydroxide in nitric acid, evaporate, and repeat the operation. As a general rule, if very exact results are wished for, this double precipitation is strongly to be recommended, as well for the peroxide of thorium, which entangles a little cerium, as for the other earths, which may carry with them a few thousandths of thorina.

	I.		II.		III.	
	Taken.	Found.	Taken.	Found.	Taken.	Found.
ThO ..	0·3670	0·3655	0·3645	0·3640	0·0508	0·0475
Ce_3O_4 .	0·0231	0·0229	0·0214	0·0370	0·9485	0·9515
LaODiO	—	—	0·0140			

We give the analysis No. III. to show the results obtained by a single precipitation.

M. Dennis (*Zeitsch. fur Ann. Chim.*, xiii., p. 412, 1897) has quite recently proposed the potassic salt of hydronitric acid for the separation of thorina from the other rare earths. This curious reaction, as a matter of fact, permits of the total precipitation of the thorina present in the mixture. Unfortunately it presents two obstacles; viz., it requires the use of a reagent which is not at all convenient to handle in any quantity, and, further, it has the grave fault of carrying down with it several hundredths of cerium which are not eliminated even by a second precipitation. In an artificial mixture containing 0·0952 of ThO and 0·927 of CeO we found, after the precipitation of the thorina by KN_3, only 0·0896 of CeO. The precipitated thorina had thus carried with it 3·34 per cent of CeO. It was then dissolved in nitric acid and precipitated with peroxide of hydrogen; the filtered solution contained 0·0028 of CeO. This experiment clearly shows that the method we propose is not only more practicable, but also more precise, than the still interesting one proposed by M. Dennis.—*Comptes Rendus*, cxxvi., No. 4.

* Commercial peroxide of hydrogen containing any considerable amount of impurities cannot be used. It must be purified by distillation; this is no longer difficult since the work done by M. Hanriot.

TESTING OF FORMALDEHYD.*

By CARL E. SMITH.

(Concluded from p. 95).

Acetone.—Three grms. of formaldehyd solution, 25 c.c. of N/1 soda solution, and 0·5 c.c. of pure acetone were heated under pressure in boiling water for forty-five minutes. A duplicate assay, omitting the acetone, was made under the same conditions. In the mixture containing the acetone a white flocculent precipitate formed on heating, and titration with sulphuric acid indicated that not more than one-third of the theoretical amount of soda had been used up. The duplicate containing no acetone gave normal figures. No attempt has yet been made to ascertain the composition of the precipitate and the cause of its formation.

Methyl Alcohol.—To 20 c.c. of a dilute aqueous solution of pure formaldehyd, 1 c.c. of commercial methyl alcohol was added and the mixture heated with soda solution, as described in the acetone experiment. The solution was assayed under the same conditions without addition of methyl alcohol:—

Without methyl alcohol .. .. 4·65, 4·65, 4·71 per cent.
With " " .. .. 4·38, 4·35 "

* Report of Research Committee DII., Committee of Revision of the United States Pharmacopœia. From the *American Journal of Pharmacy*, lxx., No. 2.

Repeated with pure methyl alcohol, 0·5 c.c. of this was added to 2·25 grms. of a concentrated solution of pure formaldehyd :—

Without methyl alcohol	37·3, 37·3 per cent.
With „ „	35·5, 35·7 „

No explanation can be made at present for the lowering of the result by the presence of methyl alcohol.

The chief disadvantages of the fixed-alkali method are interference by acetone and methyl alcohol and risk of explosion when heating under pressure. It is also subject to some variation in the results—noticed with one sample only—the causes of which cannot be satisfactorily explained at present.

Ammonia Method.—First proposed by Legler (*Berichte*, vol. xvi., p. 1333), and based on the reaction of free ammonia and formaldehyd to form hexamethylene-tetramine, $6CH_2O+4NH_3=N_4(CH_2)_6+6H_2O$.

A normal ammonia solution is usually recommended, while the decinormal is preferred by others. As the use of the latter necessitates weighing or measuring very minute quantities of formaldehyd, or else diluting a larger quantity and taking an aliquot part for assay, the work was restricted to the use of the stronger solution. Only one trial with a decinormal solution was made, which indicated that the assay would require about one hour, and that rosolic acid is not sufficiently sensitive in presence of hexamethylene-tetramine to give serviceable results until after some practice.

Experiments with N/1 ammonia solution :—25 c.c. of the ammonia solution were run from a burette into a flask and 2·25 grms. of sample added. The flask was then closed with a glass stopper thickly coated with vaseline. The mixtures were allowed to stand a definite time, and then the excess of ammonia titrated with N/1 sulphuric acid, using rosolic acid as indicator. Each c.c. of N/1 ammonia corresponds to 0·045 grm. or 0·5 per cent, when 2·25 grms. are taken.

Titrated at once after admixture	36·0 per cent.
„ after 15 minutes	37·4 „
„ „ 1 hour..	37·5 „
„ „ 2 hours	37·5 „
„ „ standing over night	37·4 „

Other trials, previously made in flasks closed with rather loosely-fitting rubber stoppers, gave somewhat variable figures, the tendency being too high results through loss of ammonia, particularly when considerable time elapsed before titrating.

Assay in presence of Acetone.—A mixture of 2·25 grms. of formaldehyd solution, 25 c.c. of N/1 ammonia, and 0·5 c.c. of pure acetone was allowed to stand twenty minutes and then titrated. The solution was assayed in a similar manner without addition of acetone.

Without acetone	34·9, 34·7 per cent.
With „	34·8, 35·0 „

Assay in presence of Methyl Alcohol.—A mixture of 2·25 grms. of formaldehyd solution (not the solution used in the preceding experiments), 0·5 c.c. of methyl alcohol, pure or commercial, and 25 c.c. of N/1 ammonia, was treated in the same manner as above, and the formaldehyd solution also assayed without addition.

Without methyl alcohol	37·4, 37·4 per cent.
With pure methyl alcohol	37·5, 37·6 „
„ commercial methyl alcohol ..	36·8, 36·9 „

According to these figures, commercial methyl alcohol may lower the result slightly, while pure methyl alcohol and acetone exert practically no influence. This method, then, is the only thoroughly reliable one of all those tried, the only drawbacks being a slight inaccuracy introduced through loss of ammonia by volatilisation, and the necessity of frequently re-standardising the ammonia solution, which loses strength rapidly. These considerations suggested to the writer a modification of this method, which obviates the need of keeping on hand a standard solution of ammonia, and reduces the volatilisation of ammonia during the manipulation to a minimum.

Ammonia Method Modified.—Dissolve 2 grms. of pure neutral ammonium chloride in 25 c.c. of water and introduce it into a flask provided with a well-fitting stopper. Add 2·25 grms. of the sample, and then run in from a burette 25 c.c. of N/1 potassium (or sodium) hydrate. Stopper the flask at once and put it aside for one-half hour. Then add a few drops of rosolic acid solution and determine the excess of ammonia with N/1 sulphuric acid, each c.c. of N/1 potassium hydrate consumed indicating 0·5 per cent of formaldehyd.

The results obtained by this modification agree closely with those obtained by the hydroxylamine, fixed-alkali, and ammonia methods. The reactions involved are as follows :—

$$NH_4Cl+KOH=NH_4OH+KCl;$$
$$4NH_4OH+6CH_2O=N_4(CH_2)_6+10H_2O,$$

or—

$$4NH_4Cl+4KOH+6CH_2O=N_4(CH_2)_6+4KCl+10H_2O.$$

The ammonia combines with the formaldehyd nearly as fast as it is liberated, and, consequently, has no chance to volatilise, and the final excess is so small that the odour is barely perceptible.

Examination of Commercial Samples.

Sample I.—Colourless, contains a white flocculent precipitate, probably para-formaldehyd, which increases on keeping, more rapidly when exposed to diffused sunlight than in the dark. Specific gravity, 1·109 at 15°/15°; free acid, assumed to be formic acid, 0·17 per cent; residue on ignition, 0·19 per cent, consisting of sodium chloride and a little sodium carbonate.

Strength, by ammonia method . ..	37·4, 37·5 per cent.
„ fixed-alkali method ..	37·3, 37·6 „
„ hydroxylamine method	37·2, 37·3 „

Sample II.—Colour faintly yellowish; contains fine particles of extraneous matter, but is free from a deposit of para-formaldehyd. Specific gravity, 1·052 at 15°/15°; free acid, 0·065 per cent; traces of acetone; residue on ignition, 0·015 per cent, consisting of copper oxide.

	Per cent.
Strength, by ammonia method..	34·6, 34·7
„ fixed-alkali method ..	35·3, 34·7, 35·6, 34·0
„ hydroxylamine method	34·4, 34·6

Cause of discrepant results by the fixed-alkali method unknown. This solution is claimed to be 40 per cent strong on the label.

Sample III.—Clear, faintly yellowish; specific gravity, 1·057 at 15°/15°; free acid, 0·07 per cent; traces of acetone; residue on ignition, 0·032 per cent, consisting of copper oxide.

Strength, by ammonia method (modified)	35·3, 35·2 p. c.
„ fixed alkali method	35·3, 35·2 „
„ hydroxylamine method ..	35·0, 35·1 „

Samples II. and III. are apparently made directly from wood-spirit, as judged by the presence of acetone, copper, and by the disproportionately lower specific gravity, indicating presence of a lighter liquid, probably methyl alcohol. These samples also have more empyreuma than is the case with Sample I.; they leave a smaller residue of para-formaldehyd when evaporated spontaneously and deposit no para-formaldehyd when exposed to daylight for nearly a month.

Tests of Identity and Purity.

The following list of tests is presented as a convenience to those who may wish to avail themselves of it as a guide in the examination of commercial products. The

details of the tests are arranged in such a manner as experiments seemed to show most practical. No test for methyl alcohol is included, as it was not found practicable to test for it in presence of formaldehyd except by tedious distillation. The pungent odour of formaldehyd completely masks the wintergreen odour obtained by the salicylic acid test, even when a large quantity of methyl alcohol is known to be present.

The solution should contain 35 to 40 per cent of absolute formaldehyd, as ascertained by the ammonia method or its modification.

It should be transparent and colourless, have a pungent odour and caustic taste, and a neutral or faintly acid reaction. Specific gravity about 1·08 at 15° C. Miscible in all proportions with water and with alcohol. On mixing with an ammoniacal solution of silver nitrate, metallic silver is separated. Heated with alkaline copper tartrate solution, cuprous oxide is separated.

If to 2 c.c. of the solution an equal volume of potassa solution and about 0·5 grm. of resorcinol be added and the mixture heated to boiling, the yellow colour which first appears gradually becomes red. (This reaction is said to be given by no other substance).

If 5 c.c. of sulphuric acid (specific gravity 1·84) be placed in a test-tube with a little salicylic acid and two drops of formaldehyd solution added, a permanent deep red colour will appear immediately.

If 1 c.c. of the solution be evaporated to dryness on a water-bath after addition of 5 c.c. of ammonia water, a white crystalline residue will remain, which, upon moistening with dilute sulphuric acid and warming, will evolve the pungent odour of the original solution. (Reconversion of hexamethylene-tetramine into formaldehyd and ammonia).

If 5 c.c. be evaporated to dryness on a water-bath, a white amorphous mass is left, which should leave no residue on ignition. (Absence of mineral impurities).

Ten c.c. should require not more than 0·25 c.c. of N/1 potassium hydrate for neutralisation, using phenolphthalein as indicator (absence of more than 0·1 per cent of formic acid).

A coil of clean platinum wire dipped into the solution and held into a non-luminous flame should not colour the flame yellow (absence of sodium), nor should it appear violet when viewed through a blue glass (absence of potassium).

Dilute the solution with three times its volume of water for the succeeding tests. No turbidity or precipitate should be caused by silver nitrate (absence of chloride); nor by barium chloride (sulphate), nor by hydrogen sulphide or potassium ferrocyanide (metals), nor by ammonium oxalate (calcium).

If 1 c.c. of formaldehyd solution be mixed with 10 c.c. of iodine test solution, and potassa solution added until the solution becomes colourless, no precipitate should be formed, nor an odour of iodoform developed (absence of acetone).

The solution should be kept in dark amber-coloured bottles, in a cool place, protected from light.

The writer is much indebted to Prof. Virgil Coblentz, in whose laboratory this work was carried on, for his great interest in these investigations, and many valuable suggestions in connection with them.

Lining Iron Pipes.—We are informed that Messrs. Henderson, Kandt, and Co., Ltd., have succeeded in coating the interior of iron pipes of small diameter with a smooth and perfect layer of porcelain enamel, and they are placing them on the market under the name of "Perlam Conduit." This announcement will be of interest to many of our readers who have hitherto been accustomed to use glass-lined tubes for the conveyance of corrosive fluids.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 17th, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

MESSRS. George F. Merson and Ernest H. Roberts were formally admitted Fellows of the Society.

STATEMENT BY THE COUNCIL.

The PRESIDENT said he was authorised by the Council to make the following statement to the Society:—

The following letter has been received by the Council:—

Letter received by the President from Messrs. Harden and Hartog.

The Owens College, Manchester, Jan, 26th, 1898.

DEAR SIR,—We beg to acknowledge the receipt of your letter of the 22nd inst. with reference to the Memorial which we had the honour of transmitting to yourself as President, and to the Council, of the Chemical Society, and to offer you our thanks in the name of the Memorialists for the consideration which it has already received.

We desire to point out that, although it was not expressly so stated in the Memorial, it was obviously the wish of the signatories, if the Council had not at present the power to propose an alteration of Bye-law V. in the sense sugested, that it should take the steps necessary to obtain that power. We gratefully recognise, therefore, the further consideration which the Council is now giving to this aspect of the question.

Would it be possible for us to be informed if it is the intention of the Council to make a definite statement with regard to the questions raised in sufficient time for the matter to be brought before the Anniversary Meeting for this year.—We are, dear Sir, your obedient servants,

ARTHUR HARDEN.
PHILIP HARTOG.

Professor James Dewar, F.R.S., &c.,
President of the Chemical Society.

The following reply had been sent that evening:—

Answer of Council.

Chemical Society, Burlington House, W., Feb. 17, 1898.

DEAR SIRS,—The Council desire me to thank you for your letter of the 26th January.

Since the presentation of the Memorial and the receipt of your letter of the 16th December, the question of the Society applying for a Supplemental Charter to enable votes at General Meetings to be given by proxy has received the anxious consideration of the Council, and in view thereof the Council has taken further legal advice on the matter.

The Council has this evening directed the President to make an announcement to the Society, which will be printed in the next *Proceedings*.—I am, dear Sirs, your obedient Servant,

JAMES DEWAR, President.

Messrs. Harden and Hartog.

Report of the Council.

The Council has submitted the question of a Supplemental Charter for legal opinion. The following was the case submitted:—

Case for the Opinion of Counsel.

On the 6th December last Counsel advised the President and Council of the Chemical Society whether under the Charter of such Society they had power to alter the Bye-Laws so as to provide for the Votes at General Meetings being given by proxy. The case then laid before Counsel and his opinion thereon are sent herewith.

The Memorial referred to in the case has now been presented to the President and Council. It was signed by over 500 Fellows, or about one-quarter of the total number. A copy thereof is sent herewith.

Together with the Memorial, a letter dated the 15th December, 1897, was received from Mr. Arthur Harden and Mr. Philip Hartog, a copy of which is also sent herewith.

Such letter contains the following passage:—

> With reference to the substance of the Memorial we wish to make one statement. We are aware that in the Charter (on page 8 of the printed text) it is provided that "at all general meetings and meetings of the Council the majority present and having the right to vote thereat respectively shall decide upon the matters propounded at such meetings" hence in order to render legal the change desired it would probably be necessary to obtain a Supplemental Charter allowing members not actually present at meetings to vote by means of balloting papers. It is in this connection material to point out that in order to obtain a revision of Bye-Laws precisely similar to that now desired by Fellows of our own Society a Supplemental Charter was quite recently obtained by the Institution of Civil Engineers:

It is upon the question of a Supplemental Charter that the opinion of Counsel is now desired.

Enquiries have been made with reference to the Supplemental Charter obtained by the Institution of Civil Engineers referred to in the above-mentioned letter. Such Supplemental Charter was obtained in March, 1896, and a printed copy thereof together with a copy of the original Charter and Bye-Laws of such Institution is sent herewith.

It appears that the circumstances under which that Supplemental Charter was granted were not analogous to the facts connected with the Chemical Society, and it is questionable whether that case can be regarded as a precedent in favour of granting a Supplemental Charter to such Society provided the Society as a whole should decide to present a petition for one.

In the first place the members of the Institution of Civil Engineers were unanimous in desiring the change. In the present case it is believed that the Fellows are not unanimous on the question, and it is not at present known whether even a majority desire the change.

Secondly, the objects of the Chemical Society and of the Institution of Civil Engineers respectively are wholly different.

The object of the Chemical Society shortly stated is the general advancement of Chemical Science by the holding of Meetings at which new discoveries are brought under discussion and the results made known to the public in a series of *Transactions*.

It is a purely scientific Society and in no sense professional, and in this respect resembles rather the Royal Society, the constitution of which requires the presence of Fellows at general meetings to enable them to vote.

The object of the Institution of Civil Engineers, on the other hand, is not merely for the general advancement of Mechanical Science; it is "more particularly for promoting the acquisition of that species of knowledge which constitutes the profession of a Civil Engineer." It holds examinations for the admission of persons desirous of becoming Associate Members, and is to a large extent a body exercising administrative functions with respect to a particular profession all over the Kingdom. Obviously therefore the considerations which would induce the Authorities to vary the regulation and management of such a body as the Institution of Civil Engineers would not be applicable in the case of a purely Scientific Society.

Thirdly, the reasons advanced for granting the Supplemental Charter to the Institution of Civil Engineers do not exist in the case of the Chemical Society. The Institution of Civil Engineers stated in the Petition for such Supplemental Charter whereas when their Charter was granted (in 1828) the number of Members of all classes was 156, that—

> On the 2nd day of January 1896 the number of Members of all classes was 5969 the prescribed number of members of the Council is no longer sufficient to enable the Institution to place on the Council an adequate number of representative men having regard to the total number of members and the scope of all branches of engineering science as now taught and practised throughout the realm and the number of members residing in or near the Metropolis now forms a comparatively small portion of the whole number and a large proportion cannot now be reasonably expected personally to attend General Meetings &c. &c.

In the case of the Chemical Society it cannot be alleged that the number of the Members of the Council is inadequate having regard to the total number of the Fellows, the present number being 37 (including 15 vice-presidents who have been presidents) out of a total number of about 2100 Fellows. Under the existing Bye-Laws of the Institution of Civil Engineers the number of the Council "shall not be less than 23 nor more than 31," the total number of members of all classes of such Institution being at the present time about 6900.

It cannot be alleged that the Council of the Chemical Society has not contained from its foundation an adequate number of representative men. In fact the Memorial in favour of an alteration in the bye-laws states:—

> It is of course recognised that a custom has grown up of choosing a certain proportion of the officers and Council from among the Fellows who reside in the provinces.

It cannot be alleged that the number of Fellows of the Chemical Society residing in or near the Metropolis forms a comparatively small portion of the whole number, or that a large proportion cannot now be reasonably expected personally to attend General Meetings. There has not in recent years been any material increase (see Table of Statistics below) in the proportion of the number of Fellows who do not reside in or near the Metropolis as compared with the whole body, and there is the further fact that whereas the object of the Society above mentioned has remained unchanged since the date of its charter in 1849, means of transit and communication with the other parts of the kingdom have since that date become greatly facilitated.

Statistics of the Society.

	No. of Fellows.	Resident in London District.		Not resident in Great Britain and Ireland.		Country Members.	
			Per cent.		Per cent.		Per cent
1869	526	241	45	27	5	258	49
1871	550	255	46	36	5	269	50
1881	1090	461	42	113	10	516	48
1891	1840	625	34	289	16	926	50
1897	2100	700	33	322	16	1078	51

So far as is known there is no case in which a Supplemental Charter has been granted to an old scientific Society on the question of voting by proxy alone, where that question has not involved other considerations than the mere question of attendance of the members thereof at General Meeting, even if such body was unanimous in desiring a change in its constitution for this purpose.

Counsel is requested to advise the President and Council of the Chemical Society as to the chances of success of obtaining a Supplemental Charter.

1 If the Fellows were unanimous.

2 If there were a majority of the Fellows in favour of the proposed change, and the minority took no active steps to oppose.

3 If there should be active opposition on the part of a minority of the Fellows.

4 If there were only a minority of the Fellows in favour of the change.

Also 5 How the majority for or against the change is to be ascertained. Must it be a majority of the whole of the Fellows or a majority of those voting at a General Meeting.

The following is the opinion of Counsel.

Copy of Opinion of Mr. Cozens-Hardy, Q.C.

Opinion.

1, 2, 3, and 4. The questions raised in this case are not really questions of law, and I do not feel that any opinion I can give as to the chances of success of obtaining a Supplemental Charter can be of any value. But I may say that I think it highly improbable that the Government department, before whom the application must come, would be disposed to listen to the application unless it represented the practically unanimous view of the Fellows, and that any active opposition by even a small minority would probably be fatal. The propriety of allowing votes by proxy, or by voting papers transmitted through the post, is obviously open to reasonable doubt. It is not easy to alter the constitution of a body of this nature, except to give effect to the practically unanimous wish of the Corporators. I may add that the Supplemental Charter granted in 1895 to the Institution of Civil Engineers does not really furnish a precedent applicable to the present case. That charter dealt with various important matters of which the allowance of proxy votes or voting papers was only one. I understand also that there was no difference of opinion on the part of the Fellows of that Institution.

5. In considering whether the Fellows really desire the change proposed, I think regard must not be had only to those who are present in person at a meeting, but in some other way the wishes of the whole body must be ascertained.

HERBERT H. COZENS-HARDY.

7, New Square, Lincoln's Inn,
February 4, 1898.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *Vice-Presidents*—Professor Liveing, F.R.S., and Professor J. M. Thomson, F.R.S., *vice* Mr. Ludwig Mond, F.R.S., and Professor Roberts-Austen, C.B., F.R.S.

As *Hon. Secretary*—Dr. W. P. Wynne, F.R.S., *vice* Professor J. M. Thomson, F.R.S.

As *Ordinary Members of Council*—Messrs. E. J. Bevan, H. J. Fenton, W. Gowland, and David Howard, *vice* Messrs. B. H. Brough, J. W. Rodger, T. K. Rose, and Professor Sydney Young.

Certificates were read for the first time in favour of Messrs. Albert Abbot, B.A., Church Street, Adlington, Chorley; Henry William Coupe-Annable, University College, Sheffield; William Thomas Gidden, 108, Vicarage Road, Langley, Birmingham; Alexander Guthrie, B.Sc., Bocking, Braintree, Essex; John Heaton, 81, Garmoyle Road, Liverpool; John Shearson Hyland, Ph.D., M.A., 11, Powis Square, Bayswater; William Jones, 29, High Street, Wavertree, Liverpool; Thomas Martin Lowry, B.Sc., 28, St. Lawrence Road, N. Kensington, W.; Albert Henry Mitchell, Martin's Lane, Tiverton; Alfred James Parker, 21, East Hill, Dartford, Kent; Samuel Walker, M.A., B.Sc., 126, Gilmore Place, Edinburgh; Samuel Allinson Woodhead, B.Sc., Agricultural College, Uckfield.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

Messrs. Ernest Lionel Allhusen, B.Sc.; William Martin Bailey; Charles Edward Brittain, B.Sc.; Cecil Joslin Brooks; Benjamin S. Bull, M.A., B.Sc., Ph.D.; Charles Henry Burge; William Arthur Caldecott, B.A.; Matthew J. Cannon; Albert John Bullen Cooper; John Cooper, B.Sc.; William R. Cooper, M.A., B.Sc.; Frederick Cowling; Frederick Robertson Dodd; John R. Don, D.Sc., M.A.; Frederick W. Dootson, M.A.; Wilbraham T. A. Edwards; Frederick Gilderdale; William Setten Gilles; John Glaister, M.D.; Thomas Herbert Hills; David Homfray, B.Sc.; Atholl Francis McEwen; William Hobson Mills, B.A.; Gilbert Thomas Morgan; William Edward Moss; Herman Poole; Thomas Henry Pope; James Brown Reid; Frank Forster Renwick; William Colebrook Reynolds; William Richards; Harold Charles Sayer; Andrew Jamieson Walker, B.A.; Ernest Charles Weissmüller.

Messrs. H. T. Brown, F.R.S., F. D. Chattaway, and R. J. Friswell were appointed to audit the Society's accounts.

Of the following papers those marked * were read:—

* 14. "*Observations on the Influence of the Silent Discharge of Electricity on Atmospheric Air.*" By W. A. SHENSTONE and W. T. EVANS.

When air is submitted to the action of the silent discharge it first contracts to a remarkable extent, and then re-expands rapidly until it very nearly occupies its original volume. The residue contains a trace of nitric peroxide. The following are some of the chief conclusions arrived at from a study of the above phenomena. Oxygen, when diluted in nitrogen, as in the air, yields a very large proportion of ozone; 80—85 per cent of the oxygen present may readily be ozonised in the presence of moisture, and if great care be taken as much as 98 per cent of the oxygen may be converted into ozone.

If the ozonising of the oxygen be not pressed too far no nitric peroxide will be formed, but at a certain stage, which probably coincides, or nearly coincides, with the point at which the amount of ozone is at its maximum, nitric peroxide is formed. In the presence of nitric peroxide, ozone is rapidly destroyed by the silent discharge, and its destruction is accompanied by a considerable destruction of nitric peroxide. The presence of water vapour promotes the formation of ozone, but retards that of nitric peroxide. It was found to be impossible to ozonise the oxygen of air in the presence of a trace of nitric peroxide.

DISCUSSION.

Dr. SCOTT asked if the diminution in the quantity of nitrogen peroxide present, when all, or almost all, the ozone had again been decomposed, might not be explained by its conversion by the moist air into nitric acid, and so overlooked by the method of estimating the oxidised nitrogen which would not recognise it in this form.

Mr. SHENSTONE, in reply, said that he had not studied the effect of disruptive discharge, nor that of other diluents. In reply to Dr. ARMSTRONG, he said that the electrical conditions had been carefully regulated in the manner described in a previous communication to the Society, but all such details were now omitted in order to economise space. In the present experiments, the difference of potential at the "spark gap" was about 13,300 volts. With regard to the question asked by Dr. Scott, of course one could not be sure that *no* nitric acid had been formed when the nitric peroxide disappeared in the presence of water, but this could hardly have occurred with the dried gas, and the behaviour of dried and damp gases seemed to correspond. Moreover, the gas was always re-measured after the ozone had been destroyed, and the amount of permanent contraction did not support the idea that the nitric peroxide had been to any considerable extent converted into nitric acid.

* 15. "*Some Lecture Experiments.*" By J. TUDOR CUNDALL, B.Sc.

Conservation of Mass.—Phosphorus in a weighed and closed flask is set on fire by passing a hot wire down the hollow stem of the deflagrating spoon containing it, thus raising the temperature of the spoon to the igniting point of the phosphorus.

Graham's Law of Diffusion.—A tube is filled so that it can be filled with hydrogen and other gases, and then

connected to a filter pump by means of a closed up piece of the stem of a clay pipe, through the walls of which the gas can diffuse into the partial vacuum. The times that it takes for water to rise from one mark to another when the tube is filled with different gases are noted, and it is found that these are very nearly in the same ratio as the square roots of the densities of the gases.

DISCUSSION.

Professor ARMSTRONG observed that the apparatus used for ignition of the phosphorus was needlessly complicated. All that is necessary is a glass flask, in which a piece of phosphorus is ignited by heating the flask, which is then closed with a rubber stopper. In this simple form the experiment was well known in many elementary schools throughout the country.

* 16. "*Note on the Preparation and Properties of O-Chlorbrombenzene.*" By J. J. DOBBIE, M.A., D.Sc., and FRED MARSDEN, M.Sc., Ph.D.

In this paper the authors describe the preparation and properties of *o*-chlorbrombenzene. It is a clear straw-coloured liquid with a strong aromatic odour. It boils constantly at 204° (i V) under a pressure of 765 m.m., and does not solidify at −10°. Sp. gr. at 12·5°=1·6555 μ_D = 1·583.

* 17. "*The Ultraviolet Absorption Spectra of some Closed Chain Carbon Compounds.*" By W. N. HARTLEY, F.R.S., and J. J. DOBBIE, M.A., D.Sc.

The authors give the results of the examination of the absorption spectra of a number of organic substances differing in constitution from those previously examined by Professor Hartley and his fellow workers. The absorption spectra of substances containing closed chains, wherein four or six carbon atoms are singly linked, or two pairs are doubly linked, and of substances containing oxygen or other polyvalent atoms as links in a closed chain, were studied. The examples selected were diketohexamethylene, pyrrol, thiophene, furfurane, furfurol, pyromucic acid, and furfuramide. Tables showing measurements of the extent and intensity of the absorption by each of these substances are given. The absorption of the ultraviolet rays by solutions of some of them, and notably of thiophene, is very intense, but in no case is there any selective absorption.

The conclusion arrived at is that however intense the absorption of the ultraviolet rays may be, bodies possessing the constitution of those examined show no absorption bands.

*18. "*Note on the Absorption Bands in the Spectrum of Benzene.*" By W. N. HARTLEY, F.R.S., and J. J. DOBBIE, M.A., D.Sc.

In the earliest paper on the spectrum of benzene (Hartley and Huntington) it was described as showing six absorption bands, four of which are more persistent and stronger than the other two. Owing to the want of means to obtain a continuous spectrum, some difficulty was experienced in measuring with accuracy the weaker bands. By using a wide slit, lenses of long focus and a powerful spark, the rays are sufficiently continuous, but at a sacrifice of accurate measurement of the fiducial spark lines. One feature, however, was noticeable in spectra obtained in this way: the absorption bands were all degraded in the direction of the least refrangible rays. This was considered as suggestive of the bands consisting of groups of lines stronger and closer together on the more refrangible side, weaker and wider apart on the less refrangible. By using a very powerful spark the rays emitted by cadmium electrodes may be rendered sufficiently continuous to show these bands, and at the same time render the lines sufficiently sharp to measure them by, and from such a photograph, taken a year ago, the absorption bands have been again measured.

The results of the series of measurements taken from this photograph are compared with those obtained by Pauer by examining the vapour of benzene (*Wied. Ann.*, 1897, lxi., 362), and it is shown that his weak line λ 2670 is identical with the first absorption band, and his weak band λ 2390—2360 with the sixth absorption band observed in solutions of benzene in alcohol.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, February 26th, 1898.

Mr. SHELFORD BIDWELL, President, in the Chair.

THIS meeting was held at Eton College.

The PRESIDENT informed the Society of the resignation of one of its Hon. Secretaries, Mr. T. H. Blakesley, M.A. In doing so, he referred to the many important services rendered to the Society by Mr. Blakesley, and he expressed the Society's deep and general regret that Mr. Blakesley should now feel unable to continue them.

The Council elected Mr. W. Watson, B.Sc., to the office of Hon. Secretary.

Prof. T. C. PORTER, in whose laboratory the meeting was held, said it gave him very great pleasure to welcome the Physical Society. Eton had been most properly called "the English home of ancient classical learning." For the education of youth classics had proved itself of cardinal value. He believed that other Fellows of the Physical Society, with himself, desired that this revered tradition of classics should be maintained at Eton. At the same time they would agree with him that there was no better supplement to classics than a fair knowledge of the natural sciences.

Prof. PORTER then gave a lecture, illustrated by lantern photographs, on "*Observations on the Peak of Tenerife.*"

He also described his method for measuring the diameter of the earth.

The method consists in observing the shadow cast by the Peak upon the sea, and measuring the time that elapses between the moment when the apex of the shadow touches the sea-horizon, and the instant when it is eclipsed by the shadow of night.

Prof Porter called attention to a phenomenon hitherto unnoticed, *i.e.*, that the heated air ascending from the Peak casts a shadow, seen as a faint prolongation of that of the Peak; it rises obliquely from its apex. A photograph was exhibited, taken on a quarter-plate, in which is visible the curvature of the horizon as viewed from the altitude of the Peak.

An interesting series of unique photographs, illustrating the conformation of the Peak and the phenomena of sunrise and twilight in that latitude, was also shown. In regard to twilight, he noticed that the first approach of night, as observed looking eastward, is marked by a dark border of about five degrees width, followed by a sky somewhat lighter.

The lecturer discussed also "*A New Theory of Geyser Action.*"

The theories of Bunsen and others fail to explain why the geyser throat appears almost completely full at the end of an eruption. This immediate re-filling is the more remarkable when it is remembered that some of the geysers of the Yellowstone region discharge a million and a half gallons at each eruption, and that the eruptions may occur at five-minute intervals. Moreover, the theories generally accepted assume steeper temperature-gradients than those in a region like Yellowstone. Prof. Porter suggests that the phenomena are better explained on the assumption of an arrangement of strata such as exists in artesian-well districts; the throat or shaft of the geyser being in the position of a well communicating with a subterranean stream—the "tube" of the geyser. From the disturbed nature of the region, the tube of the geyser follows a waved course, The "shaft" rises from the

crest of the terminal wave; the other crests may be steam-traps. Since a basin-like formation is characteristic of all geyser regions, it is fair to assume that the end of the tube remote from the shaft has an outcrop in the hills that form the sides of the basin. By means of this outcrop, water continually flows into the tube. Where the tube does not sink deeply enough to attain the temperature necessary for the generation of steam, a quietly-flowing hot spring is the result. But if at any point the tube descends to underground temperatures sufficiently great, steam is formed, and is trapped at the highest point of a bend. Ultimately this steam checks the flow of water, until the accumulated head of cool water from the hills overcomes the resistance, condenses the steam, and re-establishes liquid continuity. Urged by the pressure behind it, the stream is impelled towards the geyser throat; it forces the hot water before it until equilibrium is once again restored in the tube.

Prof. Porter afterwards exhibited a Method for Viewing Lantern Projections in Stereoscopic Relief.

A slotted disc rotates in front of two lanterns. These project two stereoscopic views in rapid alternation upon a screen, in such a way that the two projections are approximately superposed. In the rim of the disc other slots are cut through which the observer looks. The arrangement of slots is such that the right or left eye is only able to see the screen at the moment when its own picture, *i.e.*, the picture from the right or left lantern, is on the screen. When the rotation is sufficiently rapid, the views appear as one, without "flicker," in stereoscopic relief.

The President proposed votes of thanks, and the meeting was adjourned until March 11.

NOTICES OF BOOKS.

Quantitative Chemical Analysis; adapted for Use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc. Lond., F.C.S., and J. Bernard Coleman, A.R.C.Sc. Dublin, F.C.S. Fourth Edition. London: J. and A. Churchill. 1897. Pp. 583.

Still further revisions, additions, and improvements have been made in this, the fourth edition of Messrs. Clowes and Coleman's well-known book. The subject-matter is divided into seven principal parts, the first five of which are again subdivided into sixteen sections. Part I., containing three sections, naturally begins at the beginning of quantitative work, and here we find full descriptions of the apparatus required, and the general rules, methods, and processes in use for the purpose of making quantitative estimations, and the calculation and entry of results. Part II. contains only one section, and is devoted entirely to simple gravimetric estimations. In Part III., divided into four sections, we read all about volumetric analysis; the apparatus and general methods are first described; after which we come to more detailed and special processes, such as alkalimetric and acidimetric methods, estimations by oxidation or by reduction, &c. Part IV., on general quantitative analysis, has four sections, but they cover a great deal of ground, and extend to over 200 pages. A good deal of attention is paid to water analysis, but we are surprised to find that the well-known and necessary combustion process for estimating the organic carbon and nitrogen in water, devised by Sir E. Frankland and Prof. Armstrong, although described as "the most accurate and trustworthy of these processes," is simply passed over, and the student referred to some other books; it is necessary for everyone having to do with modern water analysis to be thoroughly acquainted with this process, and we see no more reason why the student should be referred elsewhere for this information than for anything else in these pages. Part V. is on the volumetric estimation of gases, and consists of four sections, in which all the best known methods are described. Part VI. contains a number of reference tables; while Part VII. finishes with a few odds and ends, such as the use and preparation of compressed gases, lists of apparatus, &c.

The revised atomic weights, as re-calculated by Mr. F. W. Clarke for his work which is about to be published, have been obtained in advance, and appear in par. 774.

We congratulate the authors on having given us an eminently useful and practical volume, and we wish them still further success.

The Analysts' Laboratory Companion. By Alfred E. Johnson, A.R.C.S.I., F.I.C. Second Edition, enlarged and improved. London: J. and A. Churchill. 1897. Pp. 108.

A number of additions and improvements to this very aptly named book have been made in this edition, amongst which may be mentioned the replacing of the tables of seven-figure logarithms by those of five figures. The section devoted to weights and measures has been entirely re-written, as also have the pages dealing with the specific rotatory and cupric-reducing powers of the carbohydrates. The butter analysis and glycerin tables are also new.

The whole book abounds with useful and conveniently-arranged information, and is well interleaved with blank ruled sheets for private or additional notes.

A Graduated Course of Chemical Problems. By E. G. Bryant, B.A., B.Sc. (Lond.). Birmingham, Leicester, and Leamington: The Midland Educational Company, Lim. Pp. 31.

All the problems recently set at the Oxford and Cambridge Local College of Preceptors, London Matriculation, and South Kensington (Stages I. and II.) Examinations, will be found in this pamphlet, together with the answers and solutions. It will no doubt be useful to students who are about to present themselves for examination before any of these bodies, as it will give them a good idea of the kind of questions asked, and also the way they should shape their answers. It is essentially a book for beginners, and handy in form.

CORRESPONDENCE.

THE ATOMIC WEIGHT OF BORON.

To the Editor of the Chemical News.

Sir,—The perusal of Mr. F. P. Armitage's paper on "The Atomic Weight of Boron" (Chemical News, vol., lxxvii., p. 78) leads me to believe that some observations of my own may be of interest.

Some time ago I made a number of experiments on the behaviour of borax on ignition, paying especial attention to the loss of weight sustained at various temperatures and to the alkalinity of the residue. I came to the following conclusions:—

1. The loss of weight depends greatly upon the temperature and time of ignition. In one experiment, for example, the loss after a few minutes' ignition over a Bunsen flame amounted to 47·04 per cent, and after several hours' ignition to 47·37 per cent. In several experiments in which the blowpipe was used, a loss of over 50 per cent was noted, and when a closed crucible was used a sublimate was obtained on the lid.

2. The loss, beyond that accounted for by the water of crystallisation, is due to volatilisation of soda and of

boric acid. This is shown by the decrease in the amount of standard acid required to neutralise the residue.

3. It appears that the residue contains rather less soda than that required for the formula $Na_2B_4O_7$, and that the composition of the residue is not constant.

The use of borax for the determination of the atomic weight of boron seems, therefore, liable to be attended by two sources of error, due respectively to the uncertainty as to the composition of the hydrated and of the fused salt. It occurred to me that more trustworthy results might possibly be obtained by a series of experiments in which the alkalinity of the crystallised borax and that of the fused salt are compared together. So long as the acid required to neutralise the fused salt is not less than that required by the weight of crystalline borax from which it was obtained, it is clear that no loss of soda has been caused by ignition; and by taking into account also the loss of weight on ignition, it may be possible to select those experiments in which all water has been driven off and yet no decomposition has taken place from over-ignition.

I intend to make some experiments in this direction.—I am, &c.,

NORMAN LEONARD.

Chemical Laboratory, Guy's Hospital,
London, S.E., February 21, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Anorganische Chemie,
January 18, 1898.

Use of the Metals Sodium, Magnesium, and Aluminium in Qualitative Analysis. — Walther Hempel.—A small piece of sodium is flattened on filter-paper; this is sprinkled with the powdered substance which is to be analysed. The paper is rolled into a cylinder, and wound round with iron wire; it is then placed in the reducing flame of a Bunsen burner. The reaction is finished in a few seconds. On cooling, the spiral is unwound and the contents placed in an agate mortar. A little water dissolves the sodium salts, and the reduced metals are generally found in large enough quantities to be estimated by the ordinary methods. Sodium is not suitable where spectrum analysis is to be used; in this case magnesium or aluminium can be substituted for sodium; the method is the same, except that the powdered metal is mixed with the substance to be examined.

Quantitative Separation of Ethylene and Benzene Vapour.—E. Harbeck and G. Lunge.—In order to separate ethylene and benzene vapour in illuminating gas, first the oxygen and acetylene must be removed, and can be estimated; then the mixed gases are passed with hydrogen over platinum-black. The apparatus used is described, and a diagram given. By this process the ethylene is converted by the hydrogen into ethane, the benzene remaining unaltered. The contraction is measured. This reaction is, however, completely stopped if there is any carbon monoxide present in the mixture. Benzene can also be estimated as dinitrobenzene. When acted upon by concentrated nitric acid, or a mixture of this acid and concentrated sulphuric, it is nitrated to mononitrobenzene; but by bringing a very little benzene in contact with a large excess of acid the nitration goes further, and dinitrobenzene is formed. This is not very soluble in cold water, but easily soluble in alcohol and ether, and so can readily be separated out and estimated. At ordinary temperatures it is quite solid, and, though somewhat yellow, even with the microscope drops of mononitrobenzene cannot be distinguished.

Action of Carbon Monoxide on Platinum and Palladium.—E. Harbeck and G. Lunge.—When ethylene is led over Pt or Pd, together with hydrogen at ordinary temperatures (18°—100°), a contraction takes place, expressed by the equation $C_2H_4+H_2=C_2H_6$. The presence of carbon monoxide completely hinders this reaction, and so prevents the separation of ethylene from benzene vapour, by the method described in the former paper. This fact is explained as follows:—Both platinum and palladium form, with carbon monoxide, a compound which is stable enough to be called a true chemical compound (even though the whole of the platinum and palladium cannot be combined in a state pure enough for analysis), for the following reasons:—(1) It cannot be displaced by another gas, and even after treatment with hydrogen it will take up the same quantity of carbon monoxide as if the hydrogen were not there. (2) If the compound of carbon monoxide and platinum is heated to 250°, the carbon monoxide is given off suddenly. (3) Carbon monoxide forming a compound prevents the free surface of the platinum coming in contact with the ethylene and hydrogen, and thus stops their reaction.

Note on the Methods of Estimating the Carbon in Iron.—E. Harbeck and G. Lunge.—The amount of carbon in cast-iron and steel was estimated by several methods, the following conclusions being arrived at:—(1) The chlorine method and Corleis's method give results which agree well. (2) The method of Lunge and Marchlewski gives worse results than Corleis's method, except in the case of steel, when the copper sulphate is replaced by copper-ammonium chloride. In the case of cast-iron the gain in accuracy by using copper-ammonium chloride is so little that it is of no value. (3) The copper-ammonium chloride method requires longer time, and is much more detailed than the method of Lunge and Marchlewski, and the results of the analysis are very slightly more accurate. (4) For an accurate analysis Corleis's method is recommended, but for commercial use the method of Lunge and Marchlewski; the latter can be worked with rapidity and ease. A constant loss of about 0·03 per cent must be allowed for.

Manganese Molybdates. — Arthur Rosenheim and Hermann Itzig.—(1). Ammonium manganese molybdate was prepared by Péchard's method and analysed. The manganese was found to be present as sesquioxide, the formula being $2(NH_4)_2OK_2OMn_2O_3\,10MoO_3 + SH_2O$. (2). The potassium manganese molybdate was prepared by three different methods, and in each case appeared to have the formula $3K_2OMnO_28MoO_3+5H_2O$. The difference in the results obtained by this method and Péchard's has not been properly explained, as, in spite of many experiments, no salt of a different composition from the above formula could be obtained. The change of composition took place not only in the direct preparation, but when the ammonium potassium double salt changed into the potassium salt.

Journal de Pharmacie et de Chimie,
Series 6, vol. vii., No. 2.

Transformation of Sorbite into Sorbose by Mycoderma vini.—A paper describing a number of experiments on fermentation of the juices extracted from the berries of the *Sorbus aucuparia;* not suitable for abstraction.

A New Water Ureometer.—A. Chassevant.—This ureometer is composed of a tube graduated to tenths of a c.c., surmounted by two blown bulbs, themselves united by means of a lateral syphon, which practically makes the upper bulb a Tantalus cup. The interior arrangement of the tubes allows the gas to circulate freely through the graduated tube and the two bulbs, while preventing the liquid contained in the bulbs from entering

the graduated tube. A full description of the method of procedure for making an estimation is given, and it is claimed that—besides its application to the estimation of urea—this apparatus can be used for estimating the total nitrogen by Henninger's method, and also for making exact measurements of the volumes of gases set free by the action of one liquid on another.

Rotatory Power of Chlorhydrate of Cocaine.—H. Herissey.—These experiments have been carried out on five totally different samples, and they have given very concordant results, three of them having an identical rotatory power, viz., 71·66° in an aqueous solution of 2 grms. per 100 c.c.; under the same circumstances the rotatory power of the other two was 70·83°. At first sight these figures appear to be high, $\alpha_D = -52{\cdot}5°$ being the value given in the "Codex" and in other works. The author has carefully examined and repeated the work done by Antrick on this subject, and comes to the certain conclusion that the results obtained by him were wrongly interpreted, and that about 71·66° is the correct figure. It is possible, he admits, that the material used by Antrick in 1887 may have been of less purity than it can be obtained at the present time, and, further, he remarks that he has never experienced any cloudiness in his aqueous solutions of chlorhydrate of cocaine, an occurrence which obliged his predecessor in this matter to make use of dilute alcohol.

Series 6, vol. vii., No. 3.

On a New Ferment from the Tartrates, "Bacillus tartricus."—L. Grimbert and L. Ficquet.—An anærobic fermentation of tartrate of lime, induced by means of a few drops of a vegetable juice, incubated at 35°, was the starting-point of this research. After a number of cultivations the authors were enabled to isolate a new bacillus, to which they have given the name *Bacillus tartricus*. It is a small bacillus, about 1 to 2 μ in length, with considerable motile power; it gives no indol reaction in a peptone solution; it coagulates milk about the eighth day, and transforms nitrates into nitrites. *B. tartricus* is an active ferment of tartrate of lime, which it attacks indifferently in ærobic or anærobic cultures, but shows a preference for ærobic life.

Use of Carbide of Calcium for the Preparation of Absolute Alcohol.—P. Yvon.—This paper has already been inserted in full.

Some New Derivatives of Pyrocatechin. — H. Cousin. — The author has succeeded in obtaining trichloridised pyrocatechin, by acting on an acetic solution of pyrocatechin with an acetic solution of chlorine in the proportion of 6 atoms of the former to 1 molecule of the latter. He has also prepared two dibromised pyrocatechins as well as several mononitrated derivatives. By the action of sulphuric acid of different strengths, he obtained a monosulphuric pyrocatechin and a disulphonic pyrocatechin.

MISCELLANEOUS.

The British Fire Prevention Committee. — Mr. Robert Mond, M.A., F.R.S.E., has joined the working Executive of this Committee, with the particular view to attending to the interests of the chemical side of Fire Prevention and the questions of research work.

International Congress of Hygiene and Demography.—Referring to our recent notice of this Congress and Exhibition, to be held at Madrid early in April next, we are informed that full details can be obtained from Sir Douglas Galton, F.R.S., Parkes Museum, 74 *a*, Margaret Street, London, who is the President of the National Committee.

New Method for the Estimation of Casein in Milks.—G. Deniges.—Twenty-five c.c. of milk is placed in a 200 c.c. matrass; to this is added 5 c.c. of a cold saturated solution of oxalate of ammonium, 20 c.c. of a N/10 solution of mercuric-potassic iodide, 2 c.c. of acetic acid, and the whole made up to 200 c.c. with distilled water, and filtered. 100 c.c. of this filtrate is taken, and 10 c.c. of a solution of cyanide of potassium (equivalent to the decinormal argentic solution) is added, then 12 to 15 c.c. of ammonia. Add to this, drop by drop, N/10 nitrate of silver until the solution is permanently clouded (*q*). In another vessel place 10 c.c. of the same cyanide solution, 12 to 15 c.c. of ammonia, 10 c.c. of N/10 mercuric-potassic iodide, and 100 c.c. of water. Run in the N/10 solution of nitrate of silver until the cloudiness remains (*c*); $(q-c)$ corresponds to the casein in the milk under examination. In case $q-c$ is higher than 37, it is advisable to dilute the milk by one-half, as the operation is much more sensitive with dilute than with concentrated solutions of casein.—*Journal de Pharmacie et de Chimie*, Series 6, vol. vii., No. 1.

MEETINGS FOR THE WEEK.

Monday, 7th.—Society of Arts, 8. (Cantor Lectures). "The Principles of Design in Form," by Hugh Stannus, F.R.I.B.A.
—— Royal Institution, 5. General Monthly Meeting.

Tuesday, 8th.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
—— Society of Arts, 8. "The Making of a Stained Glass Window," by Lewis Foreman Day.

Wednesday, 9th.—Society of Arts, 8. "Linde's Method of Producing Extreme Cold and Liquefying Air," by Prof. J. Ewing, F.R.S.

Thursday, 10th.—Society of Arts, 4.30. "India and Sir Henry Maine," by Charles Lewis Tupper, C.S.I.
—— Royal Institution, 3. "Recent Researches in Magnetism and Diamagnetism," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.

Friday, 11th.—Physical, 5. "On Dynamical Illustrations of certain Optical Phenomena," by Prof. J. D. Everett, F.R.S. "On Properties of Liquid Mixtures," by R. A. Lehfeldt.
—— Royal Institution, 9. "Marked Unexplored," by Walter Frewen Lord.

Saturday, 12th.—Royal Institution, 3. "English Letter Writers," by Professor Walter Raleigh, M.A.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Manufacture of Glucose-sugar.—Can anyone give me the name and publisher of a practical chemical work on the modern manufacture of glucose-sugar? I find considerable difficulty in neutralising the sulphuric acid; chalk seems to leave a considerable quantity of free acid in the sugar.—S. Chivers.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 1998.

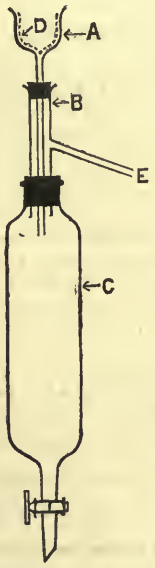
A QUICK POLARIMETRIC METHOD FOR THE ESTIMATION OF STARCH IN FLOUR, &c.

By EDWIN DOWZARD.

This method depends upon the conversion of starch into optically active bodies by the agency of diastase.

A good malt extract is obtained, such as Kepler's, or that manufactured by the Britannia Malt Extract Company; any extract, however, will do if 1 grm. of it is capable of transforming an equal weight of potato starch (as mucilage) into dextrin and maltose in the space of twenty minutes, the mixture being kept at 40·5° C. Fifty grms. of this extract is dissolved in 500 c.c. of cold water, 5 grms. of washed kaolin added, the mixture agitated, and poured on a large double filter, only that portion which passes through clear being collected.

One grm. of flour is mixed with a small quantity of cold water, 35 c.c. of boiling water is added, the mucilage kept at 100° C. for thirty seconds, then cooled down to 48° C. and treated with 20 c.c. (accurately measured) of the above malt extract solution; the mixture is maintained at 48° C. for twenty minutes, and then just brought to the boiling-point and filtered. The following piece of apparatus will be found useful at this point, as the filtration is slow.



A. Thistle-headed funnel.
B. Top portion of a fractional distillation flask.
C. Cylindrical separator.
A small circular piece of lint, D (represented by dotted lines), is placed in cup of funnel.
E is attached to a filter-pump.

The filtrate is cooled and made up to 100 c.c., a small quantity of kaolin is added, and the whole poured on a dry double filter; the optical rotation of the clear filtrate is then taken in a 20 c.m. tube, using an instrument of the Laurent half-shadow type. (It is more convenient to take the sugar divisions than the angular degrees—100 sugar divisions = +21° 40′).

Twenty c.c. (accurately measured) of the malt extract solution is diluted with 50 c.c. of water, boiled, then cooled and made up to 100 c.c.; the whole is filtered, the optical rotation of the filtrate being taken as before.

The difference between the two results is due to the starch and a small quantity of dextrine contained in the flour.

As flour contains variable quantities of dextrine it will be necessary to apply a correction which is obtained in the following manner:—One grm. of flour is converted into mucilage as before and made up to 100 c.c. with water, 1 grm. of kaolin is added, the mixture raised to 100° C., and poured on a large, dry, double filter; it is only necessary to filter enough to fill a 10 c.m. tube, in which the optical rotation is taken; this, after being multiplied by 2, is added to the malt extract figure before subtraction.

One grm. of starch in 100 c.c. = +14·4 sugar divisions (+3° 7′).

The following experiments were made with pure (wheat and potato) starch, dried *in vacuo*, and show that the above method is trustworthy.

In the first series the diastase was allowed to act for twenty minutes at 48° C. before bringing it to the boiling-point; in the second, three hours were allowed to elapse before boiling; different malt extracts were used in the two series.

The results show that after twenty minutes the optical activity is constant.

Wheat Starch. Twenty minutes at 48° C.

	Sugar divisions.		Sugar divisions.
1 grm. starch + 20 c.c. malt solution	+26·1	2 grms. starch + 20 c.c. malt solution	+40·5
20 cc. malt solution − starch	+11·7	20 c.c. malt solution − starch	+11·7
	+14·4		+28·8
1 grm. wheat starch in 100 c.c.	+14·4	2 grms. wheat starch in 100 c.c.	+28·8

Potato Starch. Twenty minutes at 48° C.

1 grm. starch + 20 c.c. malt solution	+26·1	2 grms. starch + 20 c.c. malt solution	+40·5
20 c.c. malt solution − starch	+11·7	20 c.c. malt solution − starch	+11·7
	+14·4		+28·8
1 grm. potato starch in 100 c.c.	+14·4	2 grms. potato starch in 100 c.c.	+28·8

Wheat Starch. Three hours at 48° C.

1 grm. starch + 20 c.c. malt solution	+26·7	2 grms. starch + 20 c.c. malt solution	+41·1
20 c.c. malt solution − starch	+12·3	20 c.c. malt solution − starch	+12·3
	+14·4		+28·8
1 grm. wheat starch in 100 c.c.	+14·4	2 grms. wheat starch in 100 c.c.	+28·8

Potato starch gave exactly the same results as wheat starch (after being kept for three hours at 48° C.).

(The optical rotation in all cases is taken at 16° C.).

A very simple calculation enables us to arrive at the percentage of starch in the sample operated upon. For instance—

	Sugar divisions.
1 grm. flour + 20 c.c. malt solution ..	+22·7
	+13·3
	+9·4
20 c.c. malt sol. minus flour =	+12·3
Corection for dextrin, &c. =	+ 1·0
	13·3

$$14{\cdot}4 : 9{\cdot}4 :: 100 : x$$
$$= 65{\cdot}2$$

The flour therefore contains 65·2 per cent starch.

Once the malt extract solution is prepared, an estimation of starch in flour, &c., can be completed within two hours.

ON THE

RAPID DETECTION AND ESTIMATION OF MANGANESE IN PLANTS AND VEGETABLE SOILS, BY A COLORIMETRIC METHOD.

By P. PICHARD.

When the soil contains any notable quantity of manganese, fusion with an alkaline carbonate gives a characteristic green colouration, which can be confirmed by the rose-colour produced by the addition of nitric acid.

Test for Manganese in Vegetable Soils.—The soil is dried and finely pulverised, then incinerated at a dull red-heat in a small platinum crucible, after which it is calcined with dried and powdered carbonate of soda or potash. We take from 0·5 to 1 grm. of the soil according as the colouration is more or less pronounced after the incineration; the residue is then thoroughly mixed with two parts of the alkaline carbonate. The vitreous or opaque mass produced is detached by adding a little water acidulated with nitric acid; this is placed in a test-tube, and about 0·5 grm. of minium or of binoxide of lead is added. Four c.c. of water and 2 c.c. of pure nitric acid are then poured in. Heat to boiling until the volume of the liquid is reduced by one-half; let stand until the insoluble matter has settled; the supernatant liquid should be rose-coloured if the earth contains traces of manganese.

Test for Manganese in Organic Matters.—The organic matter is dried, then rubbed fine in a mortar, incinerated, calcined with an alkaline carbonate, and treated in the manner which has been described for a vegetable soil. The incineration, however, should be carried out at a slightly higher temperature. A few decigrms. of the ash will be enough for the test. The calcination with the alkaline carbonate should be effected at a bright red-heat.

Estimation of the Manganese.—The principle consists in transforming the manganese into a permanganate dissolving to a solution of a rose-colour, and in comparing the tint of this solution with that of a typical solution containing a known quantity of manganese. The solutions are placed in graduated test-tubes of the same diameter, and distilled water is added until the colours correspond.—*Comptes Rendus*, cxxvi., No. 7.

THE

ANALYSIS OF SULPHIDE AND SULPHYDRATE OF SODIUM.

By P. DOBRINER and W. SCHRANZ.

Some little time ago we had occasion to analyse a product offerred for sale under the name of "sulphydrate of sodium." Analysis showed that it was nothing more than ordinary sulphide of sodium. We have also often had to estimate the proportion of free alkali in commercial sulphide of sodium. We think it would be of use to publish the method we employ for this class of analysis, which is characterised by great simplicity.

As is well known, the sulphydrate NaSH is produced by the action of sulphuretted hydrogen on sulphide of sodium, $(Na_2S+9H_2O)+H_2S=2NaSH+9H_2O$. On the other hand, by adding the theoretical quantity of caustic soda to sulphydrate of sodium dissolved in water, sulphide of sodium is formed, $NaSH+NaOH=Na_2S+H_2O$. It thus results that the co-existence of sulphide of sodium, of sulphydrate of sodium, and of caustic soda in one solution is *d priori* impossible. Analysis can, therefore, only have for its object the estimation of sulphide of sodium side by side with sulphydrate of sodium, and the estimation of sulphide of sodium side by side with caustic soda.

I.—*Estimation of Sulphide of Sodium in the presence of Sulphydrate of Sodium.*

Dissolve 12 grms. of the substance to be analysed in 1 litre of water, and allow about 25 c.c. of this solution to run, by means of a burette, into 45 c.c. of a $\frac{1}{10}$ normal solution of iodine, previously acidulated with 10 c.c. of a normal solution of sulphuric acid, and diluted with water to form 180 c.c.

The yellow colour of the solution should disappear. If the contrary is the case, the experiment must be repeated with a smaller proportion of the $\frac{1}{10}$ normal solution of iodide. After adding a little starch solution, we estimate by iodine solution the excess of sulphuretted hydrogen set at liberty. By multiplying the number of c.c. of iodine solution employed by 2, we obtain the percentage of sulphide of sodium present in the substance:—Let a be the percentage of (Na_2S+9H_2O) found, then the total quantity of sulphuretted hydrogen obtained from the substance will be $\frac{34}{240}a$ per cent H_2O.

On the other hand, we dissolve 6 grms. of the substance in water, treat the solution with an excess of normal sulphuric acid, boil to drive off the sulphuretted hydrogen, and titrate the excess of acidity with a normal solution of caustic soda, using phenolphthalein as indicator. The difference between the total acidity and the acidity remaining multiplied by 2, again gives the percentage of sulphide of sodium present. The figure obtained corresponds with the sulphuretted hydrogen combined with the sodium. Let b be the percentage of (Na_2S+9H_2O) found in the second operation, then the quantity of combined sulphuretted hydrogen will be $\frac{34}{240}b$ per cent H_2S.

The mixture of sulphide of sodium and sulphydrate of sodium may be considered as a mixture of sulphide of sodium and free sulphuretted hydrogen. We have found that the total amount of sulphuretted hydrogen $= \frac{34}{240}a$ per cent, and that the sulphuretted hydrogen combined with the sodium was $= \frac{34}{240}b$ per cent; the quantity of free sulphuretted hydrogen present is therefore $= \frac{34}{240}(a-b)$ per cent H_2S.

The quantity of sulphide of sodium is $= b$ per cent. According to the equation—

$$(Na_2S+9H_2O)+H_2S=2NaSH+9H_2O,$$

the $\frac{34}{240}(a-b)$ per cent ought to combine as follows—

$$\frac{240}{34}\times\frac{34}{240}(a-b)=a-b \text{ per cent } (Na_2S+9H_2O)$$

to form—

$$\frac{112}{34}\times\frac{34}{240}(a-b)=\frac{7}{15}(a-b) \text{ per cent NaSH.}$$

The substance examined, therefore, contained—

$b-(a-b)=2\,b-a$ per cent (Na_2S+9H_2O)

and—

$\frac{7}{15}(a-b)$ per cent NaSH.

II.—*Estimation of Sulphide of Sodium in presence of Caustic Soda.*

We determine the total amount of sulphuretted hydrogen by means of the iodine solution, and express the result in terms of sulphide of sodium.

Let u be the per cent of Na_2S+9H_2O found. The quantity of caustic soda combined with the sulphuretted hydrogen is then $\frac{80}{240}u$ per cent NaOH.

We determine by titration the total amount of free caustic soda and the soda combined with the sulphuretted hydrogen, and similarly express the result in terms of sulphide of sodium. The amount found $= v$ per cent Na_2S+9H_2O. The amount of free and combined sodium is, therefore, $\frac{80}{240}v$ per cent. The difference between these figures represents the amount of free soda present:—

$$\frac{80}{240}(v-u)=\frac{1}{3}(v-u)\text{ per cent.}$$

Thus, the substance contains u per cent of Na_2S+9H_2O and $\frac{1}{3}(v-u)$ per cent of free NaHO.

It results from the preceding, that the substance examined contains sulphydrite when the proportion of Na_2S+9H_2O present (found by means of the iodine solution) is higher than that found by titration with normal acid and soda. In the contrary case the substance contains free alkali.

By this method, no account of the possible presence of polysulphides, sulphites, &c., is taken. The presence of these impurities would, without doubt, complicate the analysis; but in most cases they are neglected in the analysis of sulphide of sodium.—*Zeit. für Angewandte Chemie*, p. 455, 1897.

THE DETERMINATION OF THE CARBONIC ACID IN BICARBONATES.

By G. LUNGE.

It is well known that the carbonic acid in the bicarbonates can be estimated in several manners with more or less exactness. I myself have already described three methods at different times:—(1) The method by ammonia and chloride of barium (the method by using soda and chloride of barium gives almost identical results); (2) since then, as the most exact method, the estimation in the gaseous state of the *total* carbonic acid. These two methods are described in the "*Vade mecum* of the Manufacturer of Chemical Products," by G. Lunge, p. 223; (3) a very short time since, the method of Sundström. According to this last, we add a solution of soda and baryta to the solution of the bicarbonate until one drop of the liquid gives an immediate brown precipitate with nitrate of silver by the touch test (*Zeit. für Ang. Chem.*, 1897, p. 169).

In order to determine the bicarbonate by either of these three methods, it is also necessary to know the alkalimetric titration of the bicarbonate. The third of these methods leads easily to this, but it requires a previous assay of a bicarbonate of known strength. If this precaution be neglected, one may be—as I well know—led into considerable errors. Further, this method is very useful as a control in manufacture, &c., though it is not sufficiently certain for exact determinations.

I have at last, however, succeeded in finding a means for the determination of the carbonic acid in bicarbonates—applicable only, it is true, to solid bodies, but which possesses all the necessary qualities. The operations are very simple and rapid, and give results of as great accuracy as could be desired. In this manner my new process far exceeds all the others.

This new method is of surprising simplicity; it consists only of heating the material to be analysed, and estimating the volume of the carbonic acid set free. The reasons why such a method has not hitherto been thought of are diverse. The first is that it is impossible to completely set free the carbonic acid of the bicarbonates when working with an alkaline *solution*. I have quite recently re-confirmed this opinion after a large number of experiments, in which I used vacua and modes of procedure of the most varying kind. For *solutions* it is necessary, as before, to use the old methods; for bodies in the solid state, a special apparatus is further required for the successful application of the new method. I first attempted to utilise the carbonic acid apparatus described by M. Marchlewsky and myself (*Zeit. für Ang. Chemie*, p. 229, 1891). After having placed the substance in the small disengagement chamber, the air was exhausted as thoroughly as possible; the whole was then heated in an air-bath. The carbonic acid was estimated by absorption; what remained in the apparatus was drawn out by a current of air and measured afresh; this last operation was repeated three or four times.

By this rather complicated operation, I obtained results varying from 91 to 101 per cent of the real quantity present. I cannot exactly explain the cause of these variations, in every case there are several sources of error of which I will not speak at the present time, since we cannot achieve what is required.

I have myself been astonished at the results arrived at by the apparatus now used; it resembles one of my "bulb nitrometers," or perhaps, to be more correct, one of my "gas-volumeters"; and, further, it can be made to communicate with any convenient apparatus for measuring or weighing the carbonic acid, taking care always that it has as little waste space as the "gas-volumeter"; this is always difficult to obtain with apparatus for gravimetric estimations.

A glass tube 65 m.m. long and 6 m.m. internal diameter is terminated at one end by a short length of tube of greater diameter, and plugged with a ground glass stopper; at the other end is a capillary tube 60 m.m. in length. The plug is attached to a glass rod 30 m.m. in length, unground, but of a diameter almost equal to the internal diameter of the tube; there thus remains a free space of 35 m.m. in length and of 6 m.m. in diameter, which is plugged at the capillary end by a little asbestos or glass wool. The cavity will hold about 0·850 grm. of powdered bicarbonate of soda; that is to say, an amount which, with a substance of good quality, will give a little more than 110 c.c. of carbonic acid at 0° and 760 m.m. pressure, a very convenient quantity for the universal "gas-volumeter," the graduations of which are from 1 to 30 c.c. and from 100 to 140 c.c., while the space between 30 and 100 c.c. is occupied by a bulb. If this cavity is too small or too large for any particular estimation, it can easily be altered by cutting off part of the prolongation of the plug in the first case, or by introducing more glass wool or asbestos in the second case.

The prolonged unground end of the plug is to allow of the heating of the cavity without incurring the danger of the ground part cracking, the latter, as is well known, being very sensitive to variations of temperature; we can also, without inconvenience, smear the ground part outside the air-bath with vaseline or fat, so as to make the joint perfectly tight. The heating is done *in situ* by means of an air-bath formed of a small iron crucible having two holes diametrically opposed to one another; this is covered by a sheet of asbestos through which a thermometer passes. Another sheet of asbestos is placed over the capillary tube, and this reaches to below the flame of the burner used for heating the crucible, and protects the

"gas-volumeter" from lateral heating. But in spite of this precaution it is necessary to wait at least ten minutes after each experiment before levelling and taking readings.

The operation is one of extreme simplicity. The exhausted tube is weighed, the bicarbonate introduced, and any adhering to the part near the plug carefully wiped away; the latter is adjusted with a little vaseline and the whole weighed afresh. The tube is then placed in the air-bath, and the capillary tube is connected with the lateral capillary tube of the "gas-volumeter." A vacuum is then made by lowering the mercury reservoir two or three times until a barometric vacuum is formed in the measuring tube, closing the connection on the side of the capillary tube and driving out the air; this operation should be repeated at the rate of about three times a minute.

The reservoir is again lowered, and the air-bath heated by a moderate sized flame until the thermometer indicates 260° to 270°; this will take about ten minutes. This temperature must be maintained for another three minutes, when the tap of the measuring tube must be closed. The apparatus is then allowed to cool for ten minutes, and the reservoir and reduction tube arranged so that the temperature and pressure are reduced to 0° and 760 m.m., when the volume of gas can be read off. The reduction tube should be arranged for moist gas, as the gas given off is always saturated with water. The condensation of water is, however, always so slight that it cannot have any influence on the reading. We can calculate the carbonic acid from the bicarbonate from the volume obtained, for, after having made a vacuum three times, the empty space no longer contains any measurable quantity of air. I have, however, always preferred after each reading to pass the gas into an Orsat tube, so as to be quite certain that it was completely absorbed by potash, which, I may add, always occurred. One c.c. of carbonic acid gas at 0° and 760 m.m. weighs, as is well known, 1·96633 m.grms., and this corresponds to 7·5124 m.grms. of $NaHCO_3$ (O = 16, H = 1·008, C = 12·01, Na = 23·05). We multiply the number of c.c. found by this figure, divide by the weight of the substance used, and thus obtain the proportion of bicarbonate.

If we wish to know the proportion of normal carbonate we determine the alkalimetric titration in another experiment (by means of normal acid and methyl-orange), or else the total carbonic acid by decomposition by means of hydrochloric acid, according to the method described by Marchlewski and myself.

For the purpose of controlling this new method, we first analysed a commercial bicarbonate of good quality by the old method.

By titrating with one-fifth normal hydrochloric acid, I obtained its alkalimetric value calculated into Na_2CO_3: 63·09—63·10—63·11—63·11, or a mean of 63·10 per cent (*b*).

Total carbonic acid:—

51·91	p. c. CO_3	corresponding to	125·16 Na_2CO_3
51·87	,,	,,	125·12 ,,
51·98	,,	,,	125·34 ,,
Mean 51·92	,,	,,	125·21 (*a*) ,,

According to the formula—

$$\frac{168{\cdot}136}{106{\cdot}11}(b-a) = 1{\cdot}5845\ (b-a),$$

we obtain a proportion of bicarbonate of 98·41 per cent. The possible error of 0·1 per cent in the determination of the alkalimetric value, or of the total carbonic acid (which may easily happen), would have a great influence on the proportion of bicarbonate present; in the first case the difference would be 0·16 per cent, and in the second 0·40 per cent. We thus see of what great importance the estimation of the carbonic acid is; we can obtain it with the necessary degree of accuracy by the "gas-volumeter" method.

The direct determination of the bicarbonate by the apparatus described above gives the following results:—

Substance used. M.grms.	CO_2, 0°, 760 m.m. C.c.	CO_2. M.grms.	CO_2. Per cent.	$NaHCO_3$. Per cent.
841·0	110·4	217·08	25·81	98·62
843·8	110·9	218·06	25·84	98·73
847·9	111·5	219·25	25·86	98·79
852·8	112·1	220·43	25·84	98·73
846·5	111·3	218·85	25·85	98·77
843·6	110·9	218·06	25·85	98·75
870·0	114·4	224·95	25·86	98·79

The mean of all these determinations is 98·74 per cent of $NaHCO_3$. If we reject the first, as it is rather too far from the mean of the others (which may reasonably be allowed in a first determination), the average becomes 98 76 per cent, and no single determination varies by more than 0·03 per cent. It must be admitted that this is one of the most exact methods of chemical analysis, and it is so much the more certain as it gives the substance sought for directly—that is, the carbonic acid in the state of bicarbonate. The result is much more satisfactory than that of the first one, which showed a deficit of 0·35 per cent $NaHCO_2$; it would make one think that an error of +0·05 per cent in the titration, and of −0·05 per cent in the determination of the total carbonic acid, would cover all differences, and no one can guarantee results to within +0·05 per cent. This, again, shows the great advantage of the new direct method over the old indirect method.

If we further want to know the amount of normal carbonate of soda contained in the bicarbonate, we take the alkalimetric value of the substance (which in the present case had already been done), calculate the titration value in Na_2CO_3 (=63·10 per cent), and subtract the equivalent of the bicarbonate:—

$$\frac{98{\cdot}76\times 53{\cdot}065}{84{\cdot}07} = 62{\cdot}33;$$

63·10 − 62·33 = 0·77 per cent, which is the figure sought for.

Further, to avoid an extra weighing, we might dissolve the residue contained in the small tube, and titrate it; but we might experience a small loss more easily than by weighing out a fresh quantity. As a rule, however, it is not necessary to carry out this operation.

We can also find the normal carbonate by estimating the total carbonic acid and deducting double the quantity of carbonic acid in the bicarbonate, &c. In the present case we should have 51·92 − (2 × 25·84) = 0·24 per cent CO_2 = 0·58 per cent of normal carbonate. Is this result more accurate than the preceding (0·77 per cent)? I would not care to confirm it; we can never expect great exactitude in analyses by difference.

I wish particularly to draw attention to the fact that the complete displacement of the carbonic acid in the bicarbonates, which I have just described, *does not require the carbonate of soda destined for the titration of the normal acids to be heated above* 300°; *it is preferable to heat it on a sand- or air-bath.* We can be sure, if this operation is sufficiently prolonged (for a few grms. half an hour to an hour suffices), that there is no more bicarbonate remaining, and that no oxide of sodium is yet formed, as *might* happen if the temperature reached a dull red-heat.

In conclusion, I wish to say that M. Ernest Harbeck has been of very great assistance to me in this work.

The necessary tubes can be easily made by any glass-blower; they can be obtained, however, from M. Stadelmann, Neumarket, Zurich, together with the crucible and the air-bath, for two francs.—*Zeitschrift fur Angewandte Chemie*, p. 522.

ON THE

EFFECT OF LIGHT ON THE COMBINATION OF HYDROGEN AND BROMINE AT HIGH TEMPERATURES.

By J. H. KASTLE and W. A. BEATTY.

THE combination of hydrogen and chlorine to form hydrochloric acid has been, and is still, the subject of a great deal of investigation. The effect of light, especially on this combination, has been very thoroughly studied by Draper, Bunsen and Roscoe, and others. In this connection it has been observed by Amato that a mixture of hydrogen and chlorine, if cooled to $-12°$ C., could be exposed to direct sunlight for hours without combination taking place. Such being the case it occurred to one of us (Kastle) that sunlight ought to cause the combination of hydrogen and bromine, or at least accelerate the change of these elements into hydrobromic acid, if the temperature be raised sufficiently to enable them to combine at all. So far as could be discovered, no studies of this kind had ever been undertaken. It is stated, however, that hydrogen and bromine do not combine at ordinary temperatures even in the sunlight. In order, therefore, to determine the effect of light on this reaction, a number of glass bulbs were made out of a long piece of glass tubing, in such a way as to leave one bulb connected with another in series by means of a short glass tube of small bore. Hydrogen was then passed through the series of bulbs, and, after they had been filled with the gas, the hydrogen was allowed to bubble through a small quantity of bromine, which had been purified by distillation over sodium bromide, and thus saturated with bromine it was passed through the bulbs. In this way the bulbs were filled with hydrogen more or less saturated with bromine vapour. The most remote necks of the end bulbs of the series were then sealed off in the flame of the blowpipe; and a series of bulbs thus obtained each of which contained very nearly, if not exactly, the same quantities of hydrogen and bromine. Each bulb was then sealed off in such a way as not to allow any of the gases to escape. The exact amount of hydrogen and bromine in the bulbs was not determined; it is known, however, that hydrogen was always present in excess. The hydrogen used in the experiments of series Nos. I. and II. was only purified by passing the gas through potassium permanganate and water, whereas the hydrogen employed in the experiments of series No. III. was very carefully purified by using a little copper sulphate in the sulphuric acid employed in making the gas, and by passing the gas through a solution of copper sulphate, then through one containing potassium permanganate, then through water and a solution of silver nitrate, and finally through pure water. Further, the hydrogen employed in all of the experiments herein described was not dried but used moist. Judging from certain preliminary experiments, it was thought best to work at temperatures in the neighbourhood of 200° C., and *o*-toluidine boiling at 196° C. was selected as a suitable medium in which to heat the bulbs, the manner of conducting the experiments being about as follows:—

The bulbs containing the mixture of hydrogen and bromine were placed in large, thin-walled glass tubes, containing about 50 c.c. of *o*-toluidine, and so arranged as to be mainly in the vapour of the boiling toluidine and not in the liquid itself. The large glass tubes were closed

Series No. I. Temperature 196°.

No. of Expt.	Time.	Condition.	Amount of change.
(1).	1 hour.	Sunlight.	Change nearly complete, only slight colour of bromine remaining.
(2).	2 hours.	Dark.	Very slight, if any, difference in colour of bromine. Very little change.
(3).	½ hour.	Sunlight.	Colour intermediate between (1) and (2). About half bromine combined.

Series No. II. Temperature 196°.

No. of Expt.	Time.	Condition.	Amount of change.
(1).	95 minutes.	Sunlight.	Nearly complete.
(2).	5 hours.	Diffused light.	Colour intermediate between (1) and (3), this series. About half the bromine combined.
(3).	3 hours.	Dark.	Colour about as deep as in unexposed bulbs. Very little, if any, change.

Series No. III. Temperature 196°.

No. of Expt.	Time.	Condition.	Amount of change.
(1).	15 minutes.	Sunlight (*a*).	Over 50 per cent of bromine combined.
(2). Same bulb as used in (1).	30 minutes.	Sunlight.	Almost complete—only traces of bromine left.
(3).	1 hour.	Dark.	No change observable.
(4). Same bulb as used in (3).	15 minutes.	Sunlight.	About 50 per cent change.
(5). Same bulb as used in (3) and (4).	15 minutes.	Sunlight.	Intermediate in colour between (4) and (6).
(6) *b*. Same bulb as used in (3), (4), and (5).	15 minutes.	Sunlight.	Change nearly complete—only traces of bromine remaining.

(*a*) The bulbs used in the experiments of Series No. III. were the only ones exposed to strong sunlight. During the time of the experiments of Series I. and II. the sky was frequently overcast by thin white clouds, so that the exposures to the direct sunlight were frequently interrupted.

(*b*) The bulb used in experiments 3, 4, 5, and 6 was opened and tested for hydrobromic acid. On opening the bulb dense white fumes appeared. A little water was run into the bulb and the solution thus obtained gave the well-known reactions of hydrochloric acid.

with corks bearing a long piece of glass tubing, to serve as a reflux condenser. Some of the bulbs, thus arranged, were heated in the dark and some in the sunlight. Only bulbs of the same series, of course, were compared as to the effect of light, and the amount of change was measured by the alteration in the colour of the bromine.

Appended are the results of three series of experiments.

These results certainly go to prove that light causes the combination of hydrogen and bromine, at 196° C., the amount of change being proportional to the time of exposure to light. In the dark, at 196° C., the combination of these two gases is exceedingly slow, whereas, in the sunlight, the change is fairly rapid at this temperature. Further, certain results which have been obtained would seem to indicate that light causes the combination of these elements even at 100° C., although further experiments will be necessary in order to fully establish this point.

Further, the results herein described serve to strengthen the analogy existing between chlorine and bromine, and the difference in the temperatures necessary to enable the light to cause the combination of these elements with hydrogen is simply another rough measure of their relative affinity.

A more extended investigation of this subject will be undertaken, and exact measurements made of the rate of this change, at different temperatures, in the light and in the dark. The influence of light on the combination of hydrogen and iodine, at high temperatures, will also be studied.—*American Chemical Journal*, xx., No. 2.

A DELICATE TEST FOR THE DETECTION OF A YELLOW AZO DYE USED FOR THE ARTIFICIAL COLOURING OF FATS, &c.*

By JOSEPH F. GEISLER.

THE food laws of several of the States prohibit the use of colouring-matter in oleomargarine, and, inasmuch as the presence of artificial colouring-matter in many cases constitutes the only infraction of these particular laws, simple tests for its detection are desirable. Those engaged in clarifying and decolourising oils and fats are no doubt familiar with the use of Fuller's earth as a precipitant of colouring-matter, the latter usually being precipitated without any pronounced colour reaction. Since text-books and the chemical literature, to my knowledge, do not mention the red to pink colour which Fuller's earth produces with some of the yellow azo dyes, I desire to call attention to the practicability of using this earth as a most convenient and delicate test for the detection of at least one, if not more, of the yellow azo dyes. The latter are now largely used as constituents of butter-colours, and replace annatto to a considerable extent.

While analysing a sample of a reddish-coloured butter intended for export, my attention was drawn to the large amount of colouring-matter present and the intense violet-red colour developed when I attempted to remove the colouring-matter from the clarified fat by means of Fuller's earth. The colour developed depended much upon the relative amount of Fuller's earth added, ranging from a deep violet-red to pink. All the colouring-matter giving this particular reaction was readily precipitated. The precipitate, after having been thoroughly washed with naphtha to remove the fat, presented, upon drying, a violet-red powder. Contact with alcohol immediately decolourised it, the colour reappearing upon the evaporation of the alcohol. Boiling alcohol readily extracted all the colouring-matter from the precipitate, producing a yellow solution. As obtained from the latter, the colouring-matter was found to be quite insoluble in water, sparingly soluble in hot water, re-precipitating from the latter on cooling. It dissolved with a yellow colour in concentrated sulphuric acid which, upon dilution with water, developed a bright pink to red colour. Strong mineral acids also produced a violet to pink colour. The latter reaction is familiar through the use of methyl orange as an indicator in acidimetry. True methyl orange as supplied in the market for use as an indicator, however, does not give the Fuller's earth reaction, nor is it as soluble in fats as this particular colouring-matter. These reactions with others would indicate one of the yellow azo dyes. The reactions throughout corresponded closely with a commercial yellow azo dye soluble in fats and used as a constituent of butter-colours.

Applying the Fuller's earth test to various samples of butter and oleomargarine, I found a large number of the samples to give the Fuller's earth reaction even where the samples were but lightly coloured.

In view of the fact that in certain localities oleomargarine was readily sold on the strength of the statement that only "two ounces of colouring-matter had been used per ton," and that the amount was "too small to admit of detection," it became a matter of interest to determine the limit of the Fuller's earth test and the probable amount of colouring-matter present in commercial samples of average colour. With this end in view mixtures were made with varying amounts of the yellow azo dye and pure white lard, and the test applied to the same. The mixtures were as follows:—

	Colouring-matter per kilo of lard.	Ratio.	Equivalent per ton. Ounces.
A. ..	100 m.grms.	1 : 10,000	3·2
B. ..	50 ,,	1 : 20,000	1·6
C. ..	10 ,,	1 : 100,000	0·32
D. ..	1 m.grm.	1 : 1,000,000	0·032

The latter ratio indicates fourteen grains per ton. Treated with Fuller's earth—

A developed a deep violet-red colour.
B developed a deep violet-red colour.
C developed a deep pink colour, and
D developed a pink tint.

In the latter case a half grm. of the sample spread upon a white porcelain slab developed a strong unmistakable pink upon the addition of Fuller's earth. When D was dissolved in naphtha and the Fuller's earth added to the solution, the pink appeared as a distinct ring or zone at the edge of the deposited layer of the reagent. The reaction is therefore a very delicate one.

Of the mixture A the average of several experiments showed that so minute a quantity as the 1/200th of a m.grm. still gave a pink reaction perceptible to the naked eye. Under the microscope the 1/100th part of this was still perceptible. Since the amount of colouring-matter actually present under the latter conditions was only 1/200,000,000 of a m.grm. (equivalent to 1/13,000,000,000 of a grain) the applicability of the test as a definite colour reaction under ordinary conditions is apparent. The use of as little as two ounces of the colouring-matter per ton produces a highly-coloured oleomargarine, while fourteen grains (the 10/625 part of two ounces) per ton would be barely perceptible as a faint yellow tint, but readily detected as a pink tint developed by the test.

Commercially, the yellow azo dye is generally used in conjunction with an orange variety. The latter does not give the Fuller's earth test.

For practical purposes the test is readily applied by spreading some of the clarified fat to be tested upon a white porcelain surface, and stirring into the fat a pinch of Fuller's earth and observing the change in colour. A pink to violet-red colour will appear within a few moments

* Read at the Washington Meeting of the American Chemical Society.

if any considerable proportion of this colouring-matter is present. If the experiment is performed in a glass tube it is readily preserved for court exhibits where such are desirable. The test may therefore be used as a valuable adjunct in testing for this colouring-matter in fats as well as differentiating between certain of the azo dyes.

Discussion.

C. A. Crampton.—I wish to call attention to the very valuable and *apropos* nature of this test. It seems to be a very good one, and is especially valuable because this form of colouring-matter seems to have driven out of use the old-fashioned butter colour which was made of annatto. The manufacturers say the dyes "hold up" better than annatto, by which is meant, I suppose, that they will stand time and exposure to light much better. In the paper to be presented to-morrow, I hope to show some samples of this butter-colour dye, which will illustrate the extent to which it is used in a certain class of butters.

J. F. Geisler.—It is generally claimed that these azo dyes are not detrimental to health. They are certainly used in very minute quantities.

E. A. de Schweinitz.—A number of physiological experiments have recently been made to determine the effect of these dyes, and, as a result, it is stated that they are not poisonous even when used in considerable quantities.—*Journ. Amer. Chem. Soc.*, vol. xx., No. 2, 1898.

LIQUID AIR BY THE GALLON.

At the Meeting of the Alumni Association of the Stevens Institute of Technology a very interesting exhibition of "liquid air" was made by Mr. W. H. Dickerson, M.E., representing Chas. E. Tripler, Esq., who is the inventor of the apparatus and process by which this remarkable product is readily prepared in large quantities, and who has developed the same at his own expense.

The liquid air (about 2 gallons in quantity) was brought from the works at 121, W. 89th St., New York City, very much as a can of milk might have been transported; that is, the liquid was in a zinc can placed in a wooden bucket, such as is used in transporting ice-cream, the space between the can and bucket being filled with ordinary hair-felt, such as is used in covering steam-pipes.

From this tin can the liquid air was dipped out as required with a tin ladle, exactly as milk would be served from an ordinary milk-can.

The condition of the liquid air is in fact this:—When produced it is of necessity intensely cold, because its critical temperature being about −189° F. no amount of pressure will liquefy it unless it is at least as cold as this.

When the pressure is relieved by drawing off the liquid into an open vessel, a portion at once vapourises, but in so doing cools the rest to a still lower temperature; and when so cold as this the tendency to vapourise is very moderate, so that, if the liquid air is placed in a vessel with non-conducting walls (like the tin can packed with felt in a wooden pail), it will only evaporate slowly, so that a quantity may be kept in this way for six or eight hours with only a trifling loss.

Among the interesting experiments performed on this occasion were the following:—

Liquid air was dipped out of the can and poured upon some mercury, which was promptly frozen, so that it could be shaped by hammering, exactly as a block of lead could be.

A piece of soft rubber tubing, dipped for a moment in the liquid air, became as brittle as glass, and was shattered into splinter-like fragments when struck by a hammer.

Wrought iron, cooled in like manner by liquid air, became so fragile that it was snapped with ease between the fingers, but copper and aluminum lost none of their flexibility.

An egg or piece of meat frozen by this intense cold crumbled in the hand like a piece of cracker or dry bread.

A mass of cotton or of hair-felt soaked with liquid air and lit with a match burned violently, like meal gunpowder, or like the pyrotechnic mixtures used in many "fire-works."

Poured between the poles of a powerful magnet, the liquid air clung to the poles as would iron filings, and presently formed a bridge across the space between the poles. This was due to the magnetic properties of the oxygen of which air, in part, consists.

A tea-kettle filled with liquid air boiled, giving off clouds of apparent steam without being heated, and was even made to boil more violently by the application of ice. This last will be readily understood if we remember that, as compared with liquid air, ice is a very hot substance. The appearance of steam which was seen coming from the spout of the tea-kettle or elsewhere from the liquid air, was due to the condensation of the moisture in the general atmosphere by the intense cold of the "gaseous air" into which the "liquid air" was changing.

The most impressive feature of this exhibition was the large amount of liquid air present and the ease with which it was handled.

Henry Morton, Ph.D.

[It is interesting to note that experiments with liquid air can now be exhibited in the United States on so large a scale as our correspondent has above described. The experiments, however, are quite familiar to those of our readers who have attended Professor Dewar's lectures at the Royal Institution during the past ten years].

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 17th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

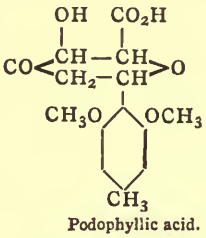
(Concluded from p. 103).

*19. "*A Chemical Examination of the Constituents of Indian and American Podophyllum.*" By Wyndham R. Dunstan, F.R.S., and T. A. Henry.

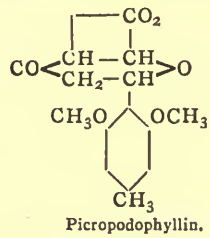
The authors find that the constituents of Indian podophyllum (*Podophyllum emodi*) and of American podophyllum (*Podophyllum peltatum*) are identical. The chief constituent is the *podophyllotoxin* of Podwyssozki and Kürsten which the authors have fully examined. It is a neutral crystalline substance (m. p. 117°), to which the authors assign the formula $C_{15}H_{14}O_6$. It is strongly lævorotatory, and acts as a powerful purgative and intestinal irritant. When heated with alkalis, it is converted by hydration into the salt of an unstable gelatinous acid, *podophyllic acid*, $C_{15}H_{16}O_7$, of which a crystalline sodium salt was obtained, and also silver and copper salts, which were analysed. This acid very readily loses water, and furnishes the crystalline *picropodophyllin* of Podwyssozki and Kürsten, which is isomeric with podophyllotoxin. It passes again into podophyllic acid when warmed with aqueous alkalis. It melts at 227°, and is optically inactive. Podophyllotoxin and picropodophyllin furnish identical decomposition products; when oxidised with nitric acid, *oxalic acid* is the principal product; when fused with alkalis *orcinol* and *acetic acid* are produced. Both substances contain two methoxyl groups and no hydroxyl. It is concluded that picropodophyllin is the

lactone of podophyllic acid, which is probably the hydroxy-carboxylic acid of *dimethoxymethyl-phenylhydro-γ-pyrrhone.*

The following formulæ are assigned to these compounds:—



Podophyllic acid.



Picropodophyllin.

The nature of the isomerism of podophyllotoxin and picropodophyllin remains to be determined. The latter substance is therapeutically inert.

The yellow colouring matter of podophyllum, called by Podwyssozki podophylloquercetin is proved by the authors to be identical with *quercetin*, the valuable yellow colouring matter of quercitron bark.

An uncrystallisable resin, *podophylloresin*, was also isolated and found to exert a purgative action.

Estimations have been made of the amount of "podophyllin" (a mixture of resins with podophyllotoxin which is used in medicine) contained in the two plants. Indian podophyllum contains from 9 to 12 per cent, and American from 4 to 5 per cent. The two resins have been proved to be equally valuable therapeutic agents. The amount of crystalline podophyllotoxin in the Indian plant varies from 2 to 5 per cent, whilst representative samples of the American rhizome were found to contain rather less than 1 per cent.

Indian podophyllum is likely to be valuable both as a drug and as a dye-stuff.

Discussion.

Mr. E. J. MILLARD asked if Professor Dunstan had noticed and could account for the smaller solubility of the resin from *P. emodi*. This was specially marked in the presence of a small quantity of an alkali when it assumed a gelatinous consistency. Since attention had been drawn to this resin by Professor Dunstan, manufacturers had prepared it in considerable quantities, and it was known commercially as the less soluble variety.

Professor DUNSTAN said, in reply, that any difference that may be observed in the solubility and other properties of podophyllin resin prepared from Indian podophyllum and that prepared from American podophyllum was probably accounted for by the different proportions in which the constituents were mixed in the resins prepared from the two sources and not by any difference in the constituents themselves.

*20. "*The Volatile Constituents of the Wood of Goupia tomentosa.*" By WYNDHAM R. DUNSTAN, F.R.S., and T. A. HENRY.

Goupia tomentosa is a large tree growing in British Guiana, where it is known as "kabucalli." The wood is hard, and is used in the colony for boat building. When freshly cut it emits a smell resembling that of valerian. By distilling the wood with water, a mixture of acids of the acetic series was obtained, from which the authors have isolated and identified *formic acid*, *isovaleric acid*, *normal caproic acid*, and *lauric acid*. A small quantity of *succinic acid* was also obtained.

*21. "*Oxycannabin from Indian Hemp.*" By WYNDHAM R. DUNSTAN, F.R.S., and T. A. HENRY.

Oxycannabin is the name given by Bolas and Francis to a crystalline substance they obtained by acting on the pharmacopœial extract of Indian hemp with concentrated nitric acid (*Trans.*, 1869, xxii., 417; CHEM. NEWS, 1871, xxiv., 77). They obtained it in the form of yellow needles melting at 176°, and represented its composition by the formula $C_{20}H_{20}N_2O_7$. In the course of the examination of the constituents of Indian hemp, the authors have prepared the substance in this way, and have also obtained it by the action of fuming nitric acid on the "cannabinol" isolated by Messrs. Wood, Spivey, and Easterfield (*Trans.*, 1896, lxix., 554) from the "charas" or resin of Indian hemp.

When quite pure, oxycannabin crystallises in colourless needles melting at 182°; it is insoluble in water, but soluble in hot alcohol, crystallising out on cooling. It sublimes when gently heated, and may be easily purified in this way. On combustion, the substance gives numbers agreeing with those required by the formula $C_{10}H_{10}NO_4$.

It does not dissolve in aqueous alkalis unless warmed with them in a closed tube. By acidifying the resulting solution, an acid is precipitated which is at present under investigation. "Oxycannabin" would therefore appear to be a lactone.

On reduction with hydriodic acid, or with tin and hydrochloric acid, oxycannabin furnishes a volatile amine. The hydrochloride of this base, though itself unstable, gives a well-crystallised platinichloride.

When heated with zinc dust, oxycannabin gives off a large amount of an inflammable gas (probably methane), and a quantity of an aromatic hydrocarbon is produced, which forms a well-crystallised compound with picric acid.

By the action of nitric acid on cannabinol, *normal butyric acid* was also produced, together with *oxalic acid*.

As the substance is thus proved to be a nitro compound, the name "oxycannabin" is inappropriate, but it would be premature to propose a new name until more is known about the constitution of the compound.

In the course of purifying cannabinol through the acetyl derivative mentioned by Messrs. Wood, Spivey, and Easterfield, the acetyl derivative was obtained in colourless crystals melting at 75°, which corresponded in composition to the formula $C_{18}H_{23}AcO$.

Discussion.

The PRESIDENT remarked that a similar investigation of the products of "oxycannabin" had been carried on for some time in the University Laboratory at Cambridge by Messrs. Spivey and Easterfield, and that they had isolated substantially the same products.

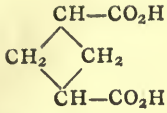
22. "*On the Condensation of Formaldehyd with Ethylic Malonate, and on Cis- and Trans tetramethylenedicarboxylic Acids* (1 : 3)." By E. W. HAWORTH and W. H. PERKIN, jun.

In a paper published some time since, (*Ber.*, 1886, xix., 1053), it was shown that when formaldehyd condenses with ethylic malonate in the presence of acetic anhydride, the principal product of the reaction is ethylic propanetetracarboxylate, $(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2$, but that at the same time a substance boiling at 208—212° is produced in small quantities which, from the results of the analysis, was thought at the time to be ethylic methylenemalonate, $CH_2{:}C(CO_2Et)_2$.

In further investigating this reaction with large quantities of material, these results have been confirmed. The condensation product contains the following substances.

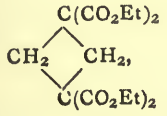
1. *Ethylic methylenemalonate*, $CH_2{:}C(CO_2Et)_2$, distils at 208° as a colourless oil which, on standing, rapidly polymerises into a hard wax-like substance, which is sometimes transparent and sometimes opaque. The polymeride, which is probably identical with the substance obtained by Zelinsky (*Ber.*, 1889, xxii., 3294), by the action of methylene iodide on ethylic malonate, on distillation yields small quantities of ethylic methylenemalonate, and considerable quantities of high-boiling oils which are at present under investigation.

When hydrolysed with alcoholic potash, the polymeride yields cis-tetramethylenedicarboxylic acid (1 : 3)—



2. An oil boiling at 234—236° (80 m.m.). Ethylic propanetetracarboxylate, $(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2$.

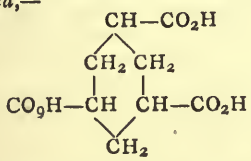
3. An oil boiling at 250—300° (40 m.m.), which evidently contains *ethylic tetramethylenetetracarboxylate*,—



since, on hydrolysis, an acid is obtained which, after elimination of carbon dioxide and etherification, yields *ethylic cis-tetramethylenedicarboxylate* (1 : 3) (b. p. 172° at 50 m.m.). This ethereal salt, on hydrolysis, yields pure cis-tetramethylenedicarboxylic acid melting at 131°.

4. When the fraction 250—300° (40 m.m.) is treated as above, it yields besides ethylic cis-tetramethylenedicarboxylate, an ethereal salt boiling constantly at 202° (30 m.m.), and from this, on hydrolysis, a crystalline acid is obtained melting at 114°.

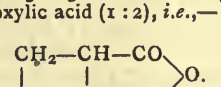
This acid, which on analysis gives numbers agreeing well with the formula $C_9H_{12}O_6,H_2O$, is probably *hexahydrotrimesic acid*,—



and in order to determine whether this view is correct, the acids formed by reducing trimesic acid are being investigated. The authors have already succeeded in preparing a crystalline tetrahydrotrimesic acid, $C_6H_7(CO_2H)_3$, which melts at about 185°, and is characterised by being very sparingly soluble in ether, but excessively soluble in water.

During the course of this research, Markownikoff's work on the action of dry sodium ethylate on ethylic α-chloropropionate has been carefully repeated (*Journ. Russ. Chem. Soc.*, 1890, xxii., 285; *Ann.*, 1881, ccviii., 333). It is found that both the cis- and trans- modifications of tetramethylenedicarboxylic acid (1 : 3) are formed in this way, and not only the trans-modification as Markownikoff states. The trans-acid (m. p. 171°), on treatment with acetyl chloride, yields the anhydride of the cis-acid (m. p. 50—51°), and this, on treatment with water, is readily converted into the cis-acid (m. p. 131°).

It is remarkable that Markownikoff, who first observed this behaviour, should have assumed that the trans-tetramethylenedicarboxylic acid, during this series of reactions, undergoes molecular change, and that the anhydride melting at 50—51° is the anhydride of tetramethylenedicarboxylic acid (1 : 2), *i.e.*,—

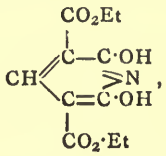


It will be shown in the detailed description of the experiments that Markownikoff's view, which has caused a good deal of confusion in the chemistry of the tetramethylenecarboxylic acids, is certainly incorrect.

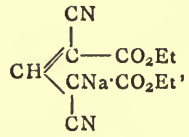
The authors are also engaged in investigating the action of methylene iodide on the disodium derivative of ethylic propanetetracarboxylate, and hope to be able soon to communicate the results of their experiments to the Society.

23. "*Formation of Ethylic Dihydroxydinicotinate from Ethylic Cyanacetate.*" By S. RUHEMANN, Ph.D., M.A., and K. C. BROWNING, B.A.

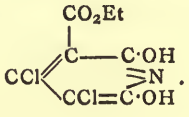
The authors give an account of their examination of the mother-liquor from the preparation of ethylic sodiodicarboxyglutaconate. They succeeded in isolating from it ethylicdihydroxydinicotinate,—



and attribute the formation of this compound to the presence of ethylic cyanacetate in the ethylic malonate. In order to verify this explanation, they studied the action of chloroform on ethylic cyanacetate in the presence of sodium alcoholate. They thus obtained ethylic sodiodicyanglutaconate,—



and prepared from it other metallic compounds and the ethereal salt itself (compare Errera, *Gaz. Chim. Ital.*, 1897, xxvii., 393). On boiling the ethereal salt with dilute hydrochloric acid, ethylic dihydroxydinicotinate (m. p. 202°) is formed. Chlorine transforms the pyridine-derivative into ethylic dichlordihydroxynicotinate, to which, from its behaviour towards phenylhydrazin, they assign the formula—



ROYAL INSTITUTION.

General Monthly Meeting, February 7th, 1898.

Sir JAMES CRICHTON-BROWNE, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

THE following were elected Members:— Miss Cecilia Ash, Mrs. Henry C. A. Baynes, Miss M. E. Bevington, The Hon. Edith M. Boscawen, Miss Alice M. Burton, The Rev. J. J. Coxhead, A. C. Cronin, R. C. Forster, Dr. Wiliam Garnett, H. Godsall, A. H. Goschen, Major-General Coleridge Grove, C.B., A. Humbert, J. J. Kincaird, Capt. Wm. N. Lister, L. M. Lowenstein, G. W. Marriott, Mrs. E. R. Merton, T. Middlemore, B. S. Ogle, P. E. Singer, G. P. Taylor, J. Thornton, and Sir Arthur Spencer Wells, Bart.

The special thanks of the Members were returned to Mr. Hugh Leonard for a donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

Melting-points of Silver and Gold.—D. Berthelot.—By means of a platinum-iridium thermo-electric cell the author has found the melting-point of silver to be 962° on an average of six experiments, and that of gold 1064° in the same manner. The first measurements of the melting-point of silver made with any degree of accuracy were by Pouillet in 1836, who made it 1000°. Becquerel in 1862 made it 960°, and that of gold 1092°. Other observers have been very near these figures, the greatest variations being only 102°.—*Comptes Rendus*, cxxvi., No. 6.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 6, February 7, 1898.

Transparence of Bismuth in a Magnetic Field.—H. Buisson.—According to the electro-magnetic theory of light the transparency of bodies is closely related to their electric resistance. It seemed interesting to try, on the same metal, if varying the conductivity also modified the transparency in the manner which might be expected. The variation of the resistance of bismuth in a magnetic field was utilised by the author. Very thin layers of bismuth were obtained by the electrolytic deposition of the metal on silvered glass, but, in spite of the action of a magnetic field of 15,000 C.G.S. units, which increased the electrical resistance by at least 60 per cent, no change in the transparency could be detected.

The Aromatic Urethanes of Conicine.—P. Cazeneuve and M. Moreau.—The energetic action of piperidine, which immediately gives urethanes by its reaction on phenolic carbonates, made it seem probable that conicine or propyl-piperidine would behave in a similar manner. Its action is, however, much less energetic; it does not give off any heat when mixed with the aromatic carbonic ethers, but requires to be boiled for the reaction to take place. By this means, and using two molecules of conicine to one molecule of carbonic ether, the authors have succeeded in preparing a number of liquid, uncrystallisable urethanes, with a viscosity increasing with the molecular weight; they are stable, and distil almost without alteration at the normal pressure; they correspond to the formula—

$$CO\begin{matrix}NC_8H_{16}\\OR\end{matrix}$$

R being an aromatic radical. They are all saponifiable with potassic alcohol, and are decomposed by SO_4H_2, giving off CO_2.

A New Coloured Reaction of Phenylhydrazine.—Louis Simon.—The solution of phenylhydrazine is warmed for some instants with a few drops of aqueous trimethylamine; a few drops of a solution of nitroprussiate of soda are then added, followed by strong potash. Immediately on the addition of the nitroprussiate a clear blue colour appears, which is decidedly deepened by the addition of the potash. A small quantity of acetic acid modifies the colouration. The reaction enables one to detect 1/50,000th of phenylhydrazine. It is very distinct with 1/10000th, but disappears after about a quarter of an hour.

Polymorphism of Fluorite.—F. Wallerant.—The author has found three distinct varieties of crystals of fluorite from different sources. The first is cubic-holohedric, the second is ternary, and the third binary.

No. 7, February 14, 1898.

A Crystallised Hydride of Dicamphene. — A. Etard and G. Meker.—Good results have been obtained by the action of sodium on the chlorhydrate of turpentine under the following conditions: — To 100 parts of dry chlorhydrate of turpentine, heated *only* to the temperature necessary to melt it, we add 15 parts of sodium, all at once, and shake frequently so as to granulate the melted sodium, and thus place it in good contact with the liquid chlorhydrate. It is of great importance to carry out this operation slowly, so as to prevent any rise of temperature favourable to excessive polymerisations. This control of temperature gives the best chance of a good return. The action of the sodium being finished, instead of distilling in the presence of salt and a little sodium we add benzine to dissolve the carbides. The benzenic solution is washed with water, and then distilled. After the benzine is driven off we separate about 45 per cent of the liquid boiling between 150° and 160°, and 30 per cent boiling between 320° and 330°, by fractional distillation. The light fraction, made liquid by a little benzine, is shaken up with a little sulphuric acid; this acid should contain a lot of anhydride. In this manner it is easier to destroy the foreign carbides, and the hydride of camphene remains alone. Wash with a filter-pump on glass wool, with fuming sulphuric acid, then with ordinary sulphuric acid until complete decolouration, and finally with water. On distillation we obtain from 15 to 20 per cent of a magnificently crystallised substance.

Action of Cyanamide on Bromanile in the Presence of Potash.—H. Imbert.—If to a boiling aqueous solution of cyanamide holding powdered bromanile in suspension we add a few small pieces of potash, the liquid takes a beautiful green colour in transmitted light, but is yellow to reflected light. The addition of an acid, such as hydrochloric, changes the colour first to blue and then to violet.

Researches on Organic Phosphorus. — L. Jolly.—The author tried to find whether integral metalloidic phosphorus existed in the organic molecules of animal tissue, or in albumenoid vegetable matters, but his results show that such is not the case.

Rapid Detection and Estimation of Manganese in Plants and Vegetable Earths, by a Colorimetric Method.—P. Pichard.—(See page 108).

Formation of Anhydride by the Calcination of Gypsum at a High Temperature.—A. Lacroix. — In a recent communication the author described the formation of anhydrous sulphate of lime, by heating gypsum to a relatively low temperature. He has since endeavoured to transform these new sulphates into anhydrite. At a dull red-heat there is no change; but, commencing at a cherry-red heat, the layers of the dehydrated gypsum become less coherent, and when pressed by the finger forms a crystalline powder; the same happens when immersed in water. On close examination it is seen that the material has undergone a complete change, and is completely transformed into anhydrite. If the temperature is carried still higher, the anhydrite melts and recrystallises in large plates, even when rapidly cooled. Barytine ($BaSO_4$) and celestite ($SrSO_4$) both re-crystallise in the same manner with the greatest ease.

Justus Liebig's Annalen der Chemie, Vol. ccc., No. 1.

Bromsuccinic Acids. — W. Lossen. — Kekulé found that by boiling solutions of dibromsuccinic acid salts in water they decompose, metallic bromides being formed, and another product, the nature of which depends on the base. When sodium, barium, or silver salts were used, the decomposition takes place according to the following equations:—

(1). $C_4H_4Br_2O_4 + H_2O = C_4H_5BrO_5 + HBr.$
Monobrommalic acid.

(2). $C_4H_4Br_2O_4 = C_4H_3BrO_4 + HBr.$
Monobromomaleic acid.

(3). $C_4H_4Br_2O_4 + 2H_2O = C_4H_6O_6 + 2HBr.$
Tartaric acid.

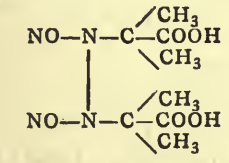
These three reactions were investigated by Lossen, with Reich, Mendthal, Riebensahm, and Schwarzenberger. They found that dibromsuccinic acid decomposes according to the equation—

$$C_4H_4Br_2O_4 + H_2O = C_2H_4O + 2HBr + CO_2.$$
Aldehyd.

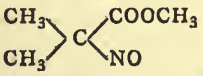
The bases potassium, barium, and calcium were used, but in no case was a reaction like that of Kekulé found to take place. The silver salt was not found to decompose in the same way as the others. The various reactions appeared to depend on the quantity of water with which the salt was boiled, but not at all or very slightly on the nature of the base. Kekulé's theory that the calcium salt is formed by boiling dibromsuccinic salts with water, which crystallises with 3 molecules of water, was proved to be incorrect. The acid formed was always a mixture of mesotartaric and racemic acids.

Hydrocinchonine. — O. Hesse. — Hydrocinchonine, which is always present in small quantity in commercial cinchonine prepared from the cinchona bark, occurs in much larger quantity in the bark of *Remijia Purdieana*. The cinchonine can be obtained pure by precipitating the mixture of cinchonine and hydrocinchonine with platinum chloride, as the cinchonine salt is crystalline, while the hydrocinchonine salt is flocculent. The alkaloid is obtained from the salt by precipitation with NH_3, and is then crystallised from alcohol. The following salts can be prepared:—(1). $(C_{19}H_{24}N_2O)_2.PtCl_6H_2$ as a yellow flocculent precipitate, from neutral platinum chloride; the precipitate changes to orange-coloured needles. (2). $C_{19}H_{24}N_2O.PtCl_6H_2$ from acid platinum chloride. (3). Four neutral sulphates crystallising with $12H_2O$, $9H_2O$, $6H_2O$, $2H_2O$ respectively.

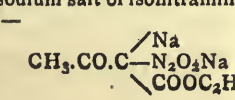
Isonitramin and Nitroso-isobutyric Acid. — M. Gomberg.—When nitrous acid acts on hydrazo-*i*-butyric acid a very explosive nitrosamine is formed, which, as it is decomposed by alkalies into isonitramin-*i*-butyric acid and oxyisobutyric acid, very probably possesses the constitution—



The decomposition products were isolated and estimated at lead salt and zinc salt respectively. The isonitraminic acid is beautifully crystalline and melts at 94° to 95°. It is best obtained by decomposing the lead salt suspended in ether by means of H_2S. The action of nitrous acid on hydrazo-*i*-butyric ester gives a product which often explodes even when mixed with ice, while the nitrate solution is being added; it must therefore be violently agitated. When this is done it decomposes without danger into N and the ester of nitroso-*i*-butyric acid—

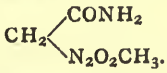


Synthesis of Nitrogen Compounds by means of Nitric Oxide—Wilhelm Traube.—This paper contains a summary of the author's work on the action of NO on a large number of compounds. He finds that all the substances which react with nitrous acid to form isonitroso-compounds also absorb NO. The substances thus produced are all strong acids, and as their sodium salts are insoluble in alcohol, these are readily obtained as the first products of the synthetical method. This consists in dissolving the original substances in absolute alcohol, adding sodium ethylate, and passing NO into the solution, when either 2 or 4 molecules are directly added on to 1 molecule of the ketone. For example, when NO is led into a solution of aceto-acetic ether in alcohol which contains 2 molecules of sodium methylate to 1 molecule of ether, the crystalline di-sodium salt of isonitramin-aceto-acetic ether is precipitated—



The acids generally form salts with the heavy metals which are slightly soluble in water, and the acids when warmed with the mineral acids decompose, yielding β-substituted hydroxylamines.

Etherification of Isonitramine Fatty Acids.—H. Sielaff.—This paper is a special part of the previous one. The isonitraminic acids are transformed into silver salt and treated with alkyliodide. Concentrated alcoholic NH_3 transforms these esters into crystalline amides such as—



The amide of methylisonitramin acetic acid, m.p. 142°; of methylisonitramin propionic acid, m.p. 150°; of methylisonitramin butyric acid, m.p. 126°. By saponification of the esters are obtained methyl-*o*-ethylisonitramin acetic acids, as syrups very soluble in water, and benzyl-isonitramin acetic acid, m.p. 135°.

MISCELLANEOUS.

The Estimation of Phosphorus in Steel.—R. W. Mahon (*J. Am. Chem. Soc.*, xix., 792—795).—The author describes a rapid method, successfully used with steels low in carbon and silicon and free from arsenic, which, he claims, will afford accurate results in about eight minutes. The procedure includes the partial neutralisation of the nitric acid and precipitation of the phosphomolybdate at a temperature near the boiling-point, and after shaking for fifteen seconds. The precipitate and filter are placed in a measured excess of caustic alkali; and the excess is determined by standard acid, with phenolphthalein as an indicator.

Reservoirs of Water in the Soil.—We take the following interesting paragraph from the *Agricultural Journal of the Cape of Good Hope* of January 20th, 1898:—"Nearly all the moisture used by plants is brought to them by the silent force of capillarity. If the soil is in proper physical condition, moisture flies upwards to the roots of vegetation from the great reservoirs in the subsoil as easily and as certainly as it runs downward by gravitation. The more the subject is studied the deeper is found the real underlying principles of successful husbandry. There should be an ample reservoir in the soil for the storage of moisture to tide over plants at critical periods. This moisture should not be in the form of free water, or that which is capable of being pushed along by its own weight, but water that is held in the soil by capillarity. Well-prepared soils are capable of holding about 30 per cent of their own weight of moisture by capillarity, and yet not contain any free or flowing water. Water may rise fully 3 feet by capillary force alone. Three feet of soil weigh 5400 tons per acre; 30 per cent of this is 1620 tons or 3,622,800 lbs., or 400,000 gallons. This is Nature's great reservoir from which plants draw moisture. If this reservoir is but 6 inches deep—the more common depth—it will hold but one-sixth as much, and hence plants grown over this small reservoir would likely droop in dry weather. Ample reservoirs, secured by means of under-drainage, culture, and tap-rooted plants, bid defiance to any reasonable drought. Having provided a supply of water, the next effort is to make as much of it as possible pass through the plant and allow as little as possible to evaporate from the surface. This is done by keeping the soil so porous and loose for 2 or 3 inches at and near the surface that water cannot pass upwards except through the plants. Beneath our feet, then, are found ever acting, kindly forces, and unnumbered forms of vegetation, all waiting to be guided and directed into channels by the skill of the husbandman."

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Society of Arts, 8. (Cantor Lectures). "The Thermo-chemistry of the Bessemer Process," by Prof. W. N. Hartley, F.R.S.
—— Society of Chemical Industry, 8. "Electrical Industries at the Foyers Waterfalls," by R. W. Wallace, Q.C.
TUESDAY, 15th.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LLD., F.R.S.
—— Society of Arts, 4.30. "The West Indies and Sugar Bounties," by Nevile Lubbock.
WEDNESDAY, 16th.—Society of Arts, 8. "The Recent History of Paper-making," by Clayton Beadle.
THURSDAY, 17th.—Chemical, 8. "The Reduction of Bromic Acid, and the Law of Mass Action," by Winifred Judson, B.Sc., and J. Wallace Walker, M.A., Ph.D. "The Action of Ferric Chloride on the Ethereal Salts of Ketone Acids," by R. S. Morell, M.A., Ph.D., and J. M. Crofts, B.A., Ph.D. "Note on the Volatility of Sulphur," by T. C. Porter. "Action of Ammonia and Substituted Ammonias on Acetylurethane," by George Young, Ph.D., and Ernest Clark.
—— Royal Institution, 3. "Recent Researches in Magnetism and Diamagnetism," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.
FRIDAY, 18th.—Royal Institution, 9. "The Bringing of Water to Birmingham from the Welsh Mountains," by James Mansergh, V.P. Inst. C.E., F.G.S.
SATURDAY, 19th.—Royal Institution, 3. "English Letter Writers," by Professor Walter Raleigh, M.A.

TO CORRESPONDENTS.

E. H. J.—The profession is over-stocked, and there is very little opportunity for a young man with no prospects or means, other than what he makes professionally, of getting more than a bare livelihood.

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(By Order)

Public Offices, Dyne Road, Kilburn, March 8th, 1898.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 1999.

PREPARATION OF LEAD-FREE AMMONIUM SALTS OF TARTARIC AND CITRIC ACIDS.

By L. de KONINGH, F.C.S.

Warington has stated that when estimating lead in tartaric or citric acid of commerce, the comparison liquid should contain the same amount of either of these acids, as otherwise the results will be quite untrustworthy. The difficulty is, however, to procure these acids free from lead or copper.

When using Warington's process (*Journ. Soc. Chem. Ind.*, 1893, 97—101) there is no absolute need for the pure *acids*, as in reality their ammonium salts are used. The writer, not having succeeded in procuring metal-free samples, has made some experiments to obtain lead-free ammonium salts, with the following results:—

By Crystallisation as Acid Tartrates.—Fifty grms. of tartaric acid were dissolved in 300 c.c. of water, and two drops of a 10 per cent solution of lead acetate were added. A little more than one half of the solution was now neutralised with ammonia, and the remainder was then added; this caused an immediate deposit of acid ammonium tartrate, which after a while became more dense and crystalline. The mother-liquor, on adding ammonia and hydrogen sulphide, gave, as might have been expected, an intense reaction for lead; but it soon appeared that the lead was far from being all in solution; then washing failed to completely remove it, and even after a litre of water had been used the washings still gave a strong lead reaction. This is very strange; for although lead tartrate is a very insoluble salt, it is said to be readily soluble in neutral ammonium tartrate, and the mother-liquor contained a large quantity of this salt. A portion of the crystalline mass was now squeezed dry between filter-paper, then dissolved in dilute ammonia and again tested, when it was found to be strongly contaminated with lead. The remainder was now dissolved in boiling water, and it separated on cooling in heavy well-formed crystals; the mother-liquor gave an intense lead reaction, and the crystals were therefore once more re-crystallised. It was now expected they would be pure, but they were still so contaminated with lead as to be perfectly unfit for use in Warington's process.

Application of Egeling's Process. — Egeling (*Ned. Tydschr. Pharm.*, 1896) has published a very handy process for the detection of traces of lead in waters. The sample is treated with hydrogen sulphide, and if any colouration should make its appearance the liquid is agitated with a little kaolin, which carries down the merest traces of lead or copper sulphide.

The writer has found this to be the best plan of freeing a solution of ammonium tartrate or citrate from lead and copper. To the solution, which should be strongly alkaline, a little strong hydrogen sulphide is cautiously added until the colour does not get any darker; a little kaolin is then added, and the whole well stirred until it has combined with the sulphides. The liquid is now filtered, and should at once be used for the comparison test. If the filtrate is yellowish, this may be remedied by agitating with purified animal charcoal. The filtrate should then once more be tested with hydrogen sulphide and, if necessary, be again shaken with kaolin.

The writer doubts whether hydrogen sulphide really removes all the lead; but, at all events, Warington's instructions that the comparison liquid should consist of an ammoniacal solution of either citric or tartaric acid, unaffected by ammonium sulphide, are properly carried out.

Efforts were made to obtain pure ammonium-hydrogen tartrate from a solution of tartaric acid strongly contaminated with lead and copper and treated by the kaolin method. Acetic acid was added, and the precipitate, after slight washing by decantation, was re-crystallised from boiling water. The result was a complete failure; and when tested it gave an intense lead reaction. This, however, may have been derived from the glazure of the porcelain dish. Solutions of ammonium citrate freed from metals by means of the kaolin process and boiled down in a beaker for some time, also had taken up a large quantity of lead. No doubt it will act, in the long run, even in the cold, so that if prepared in large quantity and kept in stock it should be again tested before use.

Warington has noticed that the colour of lead sulphide shows up much stronger in a solution of citric acid than in plain water. If, therefore, pure ammonium citrate in a solid state was at disposal, might this not be successfully used in testing water for lead in cases where the mere adding of hydrogen sulphide fails to produce a colouration?

325, Kennington Road, S.E., March 11, 1898.

THE RECENT SANDSTORM OFF THE WEST COAST OF AFRICA.

By LEONARD DOBBIN, Ph.D.

The daily papers of February 21st, in a telegram from Madrid, reported the occurrence at the Canary Islands, a few days before, of a sand-storm from the Sahara. This storm appears to have been experienced over a wide area. On the 15th February, when in lat. 22·5 N., long. 17·25 W., the R.M.S. *Roslin Castle* passed through the storm, and large quantities of fine sand fell upon the deck and adhered to the sails and rigging. By the kindness of Walter Berry, Esq., Danish Consul-General, a passenger on this steamer, who joined it at Madeira a few days later and succeeded in obtaining a specimen of the sand, a sample came into the hands of Professor Crum Brown, who handed it to me for examination.

The sample consisted of an extremely fine reddish-brown powder, which, on microscopic examination, was found to contain a large proportion of nearly white siliceous-looking particles. Treated with dilute hydrochloric acid, there was a considerable evolution of carbonic anhydride, and, on boiling for some time with concentrated hydrochloric acid, a bright yellow solution and a nearly white insoluble residue were obtained. The residue consisted essentially of silica, and a quantitative experiment showed that it amounted to 53·8 per cent of the whole.

The hydrochloric acid solution was examined for metals, and was found to contain iron, aluminium (in very small quantity), calcium, magnesium, potassium, and sodium.

The salt radicals found (in addition to silica and the salt radical of the carbonates) were those of the chlorides, sulphates (small quantity), and orthophosphates (traces only).

No traces of manganese or of borates could be detected.

Dried at 100° the powder lost 2·7 per cent of moisture.

An aqueous extract from the original powder possessed a marked alkaline reaction, indicating the presence of alkali metal carbonate.

It is unnecessary to comment upon the unpleasant nature of a shower of this fine alkaline dust.

Mr. Berry has been good enough to add the following particulars:—

The R.M.S. *Roslin Castle*, Capt. de la Cour Travers, entered the dust cloud 5—10 miles off Cape Blanco, and

continued in it for nearly two days. It extended many hundred miles out to sea, and so dense was it that the objects on deck could not be clearly distinguished, officers and men suffering great discomfort in their eyes. The vessel was in no inconsiderable danger passing through the Canaries. There was still a slight fall, even at Madeira, on the 17th February.

On the 15th, at Funchal, the sun had the appearance of the moon, and what was thought to be a fog of an unusual and unprecedented character hung over the island.

The dust penetrated everywhere, decks and spars being coloured brown.

Although a gale was blowing at Madeira, there was no wind when passing through the dust.

ON THE CONJECTURAL GROUP OF INACTIVE ELEMENTS.

By JULIUS THOMSEN.

THE discovery of argon, as well as certain small communications by Lecoq de Boisbaudran (*Comptes Rendus*, cxx., p. 361) and Sedgwick (CHEMICAL NEWS, lxxi., p. 139), lead me to make known certain ideas which have forced themselves upon my attention years ago, but which I did not wish to publish at an earlier date in order to encumber Science with hypotheses which could not be sufficiently controlled by experience. But, now the existence of inactive elements is under discussion, I am no longer disposed to keep back my views on this subject.

In the periodic system of the elements we know that in each series of the elements the valency alters with the increasing atomic weight, begins with one, increases to a maximum (four or upwards), and then returns, so that the first and last member of each series is each univalent.

With the increasing atomic weight the electro-chemical character of an element varies; each series commences with a strongly electro-positive element, and concludes with one strongly negative, whilst the intermediate members present feebler electrical characters.

But immediately upon the strongly electro-negative element of one series there follows the strongly electro-positive initial member of the next series: this is a very surprising phenomenon, for, whilst the electrical character varies only gradually in each series, there appears a sudden change from a strong electro-negative to a strong electro-positive when the atomic weight increases by a few units of which that of the last member of a series differs from the atomic weight of the first member of the next series.

If the chemical character of the elements is altogether a periodic function of the atomic weights, as we can scarcely doubt, such a function must also obey their general laws. Now the periodic functions—the transition from negative to positive values, and inversely—must take place either by way of null or of infinity; in the former case the transition is gradual, but in the latter case sudden; the former case corresponds to the gradual modification of the electrical character with the increasing atomic weight in the individual series of elements, but the latter case corresponds to that of the transition from one series to the next.

Hence it may be supposed that the transit from one series of elements of the periodic system to the next takes place by way of an element the electric character of which may be designated as $\pm\infty$, *i. e.*, it is electrically indifferent. The valency of such an element would be null; it would, in this direction, form the transition between the two successive monovalent elements, the electro-negative and the electro-positive.

Assuming now that the transition between the various series of elements, as I have arranged them in my treatise the "Systematic Grouping of the Elements," is formed by such elements, it follows directly that their atomic weights, expressed in whole numbers, would be—4, 20, 36, 84, 132, 212, and 292, and the periodic system would then contain seven series of elements, that is to say:—

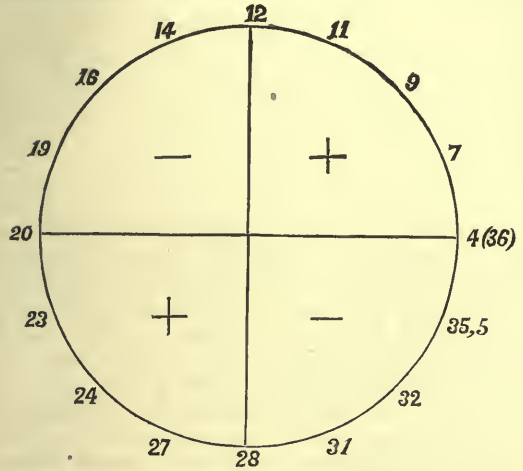
In the series 4—8, containing respectively 17 and 31 elements, only the first and the last members are included in the table, which is sufficient for orientation; in the last series only two elements, thorium and uranium, are hitherto known.

In this form the periodic system offers essentially new points for theoretical considerations. Proceeding from the hypothesis of the unity of matter, which, in defiance to all attacks, cannot be expelled from the thoughts of the investigators of Nature, the existence of inactive elements may be simply explained in this manner—that in an especial, simple, and closed arrangement of the primary elements, molecules may originate which present no points for attack, and can therefore form no stable compounds, but obey only the general laws of gravitation. It cannot surprise us that the atomic weights of such substances appear with a simple numerical relation as here assumed multiples of 4. An increase or decrease of the mass (of the atomic weight) of such a portion of matter elicits the chemical and electrical properties, and in such a manner that by an increase of the atomic weight of the inactive substance there arises an electro-positive element, whilst a decrease of the atomic weight yields an electro-negative element, and the electric character is manifested with the greatest intensity in this first modification of the mass of the inactive element. By means of this reception or loss of matter the power of chemical combination is simultaneously developed, and the substance becomes monovalent or polyvalent, according to the extent of the modification of the atomic weight until this reaches the half-interval between the two inactive elements which limits each series of elements; from that point the valency declines again until the substance passes over through a monovalent element into the next inactive element. If considered in this manner the change of the chemical and electrical character of the elements is a continuous periodic function of the mass, *i.e.*, of the atomic weight. But concerning the kind of function, concerning its mathematical expression, the arrangement above given affords an exposition free from ambiguity.

The alteration of the electric character of the elements, in part suddenly by null and in part by $-\infty$ and $+\infty$, as also the growth of the valency from null to a maximum and its return to null by the progressive change of the atomic weight, draws our thoughts involuntarily to the trigonometric and elliptical functions,—since here also there appear the same phenomena, with the increasing magnitude of the arc or of the angle. If, *e. g.*, we inscribe the elements of the first group from lithium to chlorine in a circle the circumference of which is 32, and in such a manner that we set out from the atomic weight 4 of the first inactive element, we obtain a scheme in which the elements are shown by their

I. Hydrogen	0				1								4	
II. Lithium—Fluorine	4	7—9			11	12		14		16		19	20	
III. Sodium—Chlorine	20	23	24		27	28		31		32		35·5	36	
IV. Potassium—Bromine	36	39	40							79		80	84	
V. Rubidium—Iodine	84	85	87							125		127	132	
VI. Cæsium	132	133	137										212	
VII. ——	212												292	

atomic weights :—We see at once that the elements of the first and third quadrant are electro-positive, but those of the second and fourth electro-negative. We have the strongest electrical character in the elements which lie nearest the horizontal diameter, *i. e.*, attach themselves to an inactive element, 4 (30) or 20, consequently in this case to lithium and chlorine, sodium and fluorine, whilst carbon and silicon—with an undecided electrical character — attach themselves to the perpendicular diameter.



This behaviour reminds us, without doubt, of the function cotang. x, and if we call the atomic weight a, the electro-chemical character, e, of all the elements of this group may be expressed by—

$$e = \text{cotang.}\ \frac{a-4}{16}\pi.$$

As a matter of course this formula cannot express the absolute value of the electrical character of the elements, but only the general course of its dependence on the atomic weight.

With the increase of the atomic weight the valency of the elements is altered; it rises in the first quadrant from null to a maximum,—*e. g.*, 4,—passes back to null in the second, reaches its maximum again in the third quadrant, and returns finally in the fourth to null. The rise and fall of the valency with the growing atomic weight of the elements is consequently expressed by the + and − marked in the quadrants.

These considerations also give us information on the mathematical expression for the dependency of the valency on the atomic weight. Such a course would be given in its simplest form by $m\ (\sin\ x)^2$ if m is the maximum of the valency hence designated by 4 in the above group of elements. Hence we may assume that the formula—

$$v = 4f\left(\sin\frac{a-4}{16}\pi\right)^2,$$

if f denotes a function of the square of the same which would express the rise and fall of the valency for all the values of a situate between 36 and 4.

For the second main group of the elements with atomic weights between 36 and 132 (potassium to iodine) it is easily intelligible that a similar relation would appear between the atomic weight on the one hand, and the electric character and the valence of the elements on the other, only that the constants would obtain a different value. The angle must be expresssed by—

$$\frac{a-36}{48}\pi.$$

Possibly there would be substituted an elliptical arrangement of the elements for the circular. In the same manner must be conceived the relation of the elements of the third main group with atomic weights from 132 to 152, of which hitherto only the first half is partially known. Concerning the first small group with atomic weights from 0 to 4, it must be assumed that only includes hydrogen, which would be in harmony with the small atomic weight (4) of first inactive element.

By the assumption of the existence of the inactive elements here in question with atomic weights 4, 20, 36, 84, 132, 212, and 292, with an indifferent electro-chemical character and a valence =0, and by the arrangement of the elements which I have indicated, the periodicity in the property of the elements appears as a continuous function, and at the same time we perceive the cause of the arrangement in groups each of two series, since each group corresponds to the four quadrants of the circular arrangement. We may therefore assume that by these supplements the periodic system has received a form which will essentially facilitate a future mathematical treatment of the entire problem. — *Zeitschrift für Anorganische Chemie*, vol. ix., p. 283.

ON THE

SPECTROGRAPHIC ANALYSIS OF SOME COMMERCIAL SAMPLES OF METALS, OF CHEMICAL PREPARATIONS, AND MINERALS FROM THE STASSFURTH POTASH BEDS.

By WALTER NOEL HARTLEY, F.R.S., and HUGH RAMAGE, F.I.C., A.R.C.Sci.I., Royal College of Science, Dublin.

As already published (*Proc. Roy. Soc.*, 1896, lxx., p. 393, and *Trans.*, 1897, p. 281), we have found gallium to be a common constituent of many iron ores, and have separated it from blast-furnace metal smelted at Middlesbrough. Lately, we have been led to examine the steel obtained from the same metal by the basic Bessemer process, and rolled into rails. Considering that alumina in a very high degree of purity is prepared from Irish bauxite and reduced to aluminium in the electric furnace, we have carefully examined samples kindly supplied us by the British Aluminium Company, Limited, of (1) pure alumina from the Company's works at Larne, Co. Antrim (the process of preparation has been described by Mr. James Sutherland, *Engineering*, lxii., p. 291); (2) the residual ferric oxide, or "red mud"; and (3) commercially pure aluminium, containing about 99·75 per cent of the metal.

Alumina and Aluminium.—In 1, the pure alumina, we found sodium, potassium, copper, gallium, iron, lead, and traces of indium. In 2, the "red mud," sodium, potassium, calcium, copper, silver, gallium, iron, nickel, chromium, and lead. No. 3, the metallic aluminium, contained sodium, potassium, calcium, copper, silver, gallium, iron, manganese, lead, and traces of indium.

It will thus be seen that a trace of iron, and some of the silver, copper, and gallium, pass from the bauxite, which is obtained from mines at Glenravel, Co. Antrim, into the very carefully prepared alumina manufactured at Larne, and finally makes its appearance in the aluminium reduced at Foyers, Inverness-shire.

The following remarks may be aptly made in connection with the results obtained:—First, the aluminium is not stated to be present, because it gives a spectrum in the oxyhydrogen flame only under certain conditions which are not always under control, and as the aluminium was known to be the chief constituent of the majority of the substances, it was not necessary always to state it as such. Silica and titanic acid are not recognised by this method of examination,

Secondly, all the results were obtained in exactly the same way from a weighed quantity of each substance.

Thirdly, the alkali metals, calcium, iron, and copper, are not substances accidentally present in the flame, since we have made a variety of experiments at different times, and have no difficulty whatever in obtaining spectra free from iron and copper. We have no greater difficulty in obtaining spectra free from from potassium and calcium lines, and with those of sodium so reduced as to be nothing more than a mere suggestion of the element being in the flame.

It will thus be understood that every element mentioned is actually a constituent of the metal or compound examined. It is of importance that this should be noted.

Railway Metal.—We made an examination of drillings from steel rails from the North Eastern Steel Co.'s works at Middlesbrough. They contained sodium, potassium, calcium, copper, silver (a trace), gallium, manganese, and lead (a trace).

It is interesting to note that steel rails may contain small quantities of metal not hitherto suspected of being alloyed in commercial iron of such purity, as, for instance, copper, silver, gallium, and lead. Nickel and chromium, although contained in the crude, or "mixer metal," from the blast furnaces, are present in more minute proportions in the steel made by the basic Bessemer process.

The systematic examination of railway metal by such an analytical method as this would prove of much interest, and might become of actual practical importance.

Salts of Aluminium.—In endeavouring to trace the passage of the rarer metals from aluminous ores into various commercial salts of alumina, we made experiments on various laboratory samples of alum and crude alumino-ferric cake.

These we will describe as follows:—

1. Ammonium alum, crystals.
2. Potassium alum, crystals.
3. Ground alum.
4. Ordinary lump alum.
5. Granulated alum.
6. *Turkey-red* alum.
7. Alumino-ferric cake.

No. 1, the ammonia alum, contained sodium, potassium, a trace of calcium, copper, gallium, thallium, and a trace of iron. No. 2, the potassium alum, contained, in addition to the metals known to be present, rubidium, thallium, a trace of iron, and nickel.

In each of the samples numbered 3, 4, 5, and 6, the following four metals were detected:—Sodium, rubidium, calcium, and thallium.

The rubidium lines were strong in the *Turkey-red* alum.

No. 7, the alumino-ferric, contained sodium, calcium, copper, gallium, thallium, iron, nickel, a trace of manganese, chromium, and lead.

We considered that it was desirable that larger quantities of some of these salts should be operated upon, and the gallium separated by the method described by Lecoq de Boisbaudran, which consists in precipitating it as ferrocyanide by the addition of potassium ferrocyanide to a very strongly acidified solution of the salt made by adding three times its volume of concentrated hydrochloric acid to the aqueous solution. The purity of the ferrocyanide was first proved before being used for this test.

Fifty grms. of each of the samples Nos. 1, 2, 5, and 6 were tested.

The ferrocyanide precipitates were collected on filters of ashless paper and burnt.

The precipitate from No. 1 yielded silver, nickel, and a trace of manganese, in addition to the metals previously observed in this salt, but without the thallium, which was thus seen not to be carried down.

The other samples, which are potassium alums, all yielded precipitates containing sodium, rubidium, calcium, copper, gallium, thallium, and cæsium.

Ten grms. of the alumino-ferric, treated in like manner, yielded, in addition to the above-mentioned metals, nickel, a trace of manganese and lead.

It will be noticed that rubidium, cæsium, gallium, thallium, copper, nickel, and silver, are all thrown down by potassium ferrocyanide when it is added to a strongly acidified solution. Whilst the gallium comes from the aluminous ore, bauxite, the thallium comes from the sulphuric acid. We have detected it in the pyrites used, and with it a trace of indium.

Rubidium and cæsium, it was conjectured, had been introduced with potash salt, and it was considered desirable to examine not only the sources of potash, but also other minerals obtained from the Stassfurth potash beds. The results gave an emphatic negative to this supposition.

The Stassfurth Minerals.

The following were examined:—

Kainite, $MgSO_4,KCl+3H_2O$.
Tachydrite, $CaCl_2,2MgCl_2+12H_2O$.
Sylvine, KCl.
Kieserite, $MgSO_4+H_2O$.
Stassfurthite, $MgCl_2,6MgB_2O_4,B_2O_3$.
Epsomite, $MgSO_4+7H_2O$.
Rock salt.

Every specimen contained both sodium and potassium, but neither rubidium nor cæsium. All but Stassfurthite contain calcium; all but sylvine and rock salt contain magnesium also. Iron is a constituent of all. Strontium and a trace of manganese are found in tachydrite; strontium and a trace of nickel in epsomite; boric oxide bands were very strong in the Stassfurthite spectrum, which also showed a trace of copper to be present.

We have no doubt whatever, now, that the rubidium and cæsium come from the bauxite, whether Irish or French, and from shale, in which we have also found these elements associated with potassium and lithium. This fact is remarkable.

The shale used in the manufacture of the alums is the richest mineral in gallium, sodium, potassium, and rubidium, and poorest in nickel and silver. Specimens of Irish bauxite and shale have been found to be equally rich in copper, and French bauxite richest in lithium and silver.

To trace the cæsium satisfactorily it would be necessary to work on larger quantities of material, and separate—at least partially—the other alkali metals, because the continuous spectrum given by these when present in large proportion masks the weaker lines of other elements.—*Transactions of the Chemical Society*, 1897.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several

samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined by us, all were found to be clear, bright, and well filtered.

We have again to record a great deficiency in the rainfall; although rain has fallen at Oxford on sixteen days out of the month, the total amount is only 1·19 inches; as the average for the last thirty years is 1·76 inches, we have a deficiency of 0·57 inch on the month, bringing the present deficiency for the year to 1·91 inches.

Our bacteriological examinations of 232 samples have given the results recorded in the following table; we have also examined 31 other samples, from special wells, standpipes, &c., making a total of 263 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	490
New River, filtered (mean of 23 samples) ..	22
Thames, unfiltered (mean of 24 samples) ..	2119
Thames water, from the clear water wells of five Thames-derived supplies (mean of 114 samples)	24
Ditto ditto .. .. highest	258
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	1017
River Lea, from the East London Company's clear water well (mean of 23 samples) . ..	23

The two Rivers supplying London with water are in remarkably good condition for the time of year. This is no doubt due to the abnormally low rainfall. The excellent condition of the filtering and storage works of the Companies is shown by the high quality of the water revealed by the enclosed analyses.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON A COMBINATION OF PHOSPHORIC ANHYDRIDE WITH BENZENE.

By H. GIRAN.

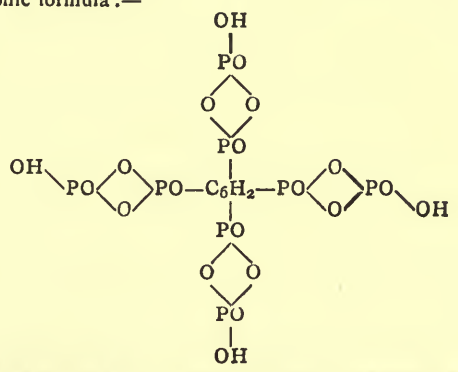
The formation of sulphonic acids by the action of fuming sulphuric acid on various organic compounds, led me to think that phosphoric acid might also give rise to bodies analogous to these sulphonic acids. For the purpose of verifying this hypothesis in one particular case, I heated a mixture of two parts of phosphoric anhydride with three parts of benzene (or one molecule of P_2O_5 and 3 molecules of C_6H_6) for four or five hours in a sealed tube at from 110° to 120°. A solid brick-red, but very unstable, substance was produced, which dissociated rapidly in free air, but which could be preserved in an atmosphere of benzene. In the presence of water it decomposes into benzene and phosphoric acid, but it is soluble in alcohol. This solution slowly attacks carbonate of baryta, and changes after the lapse of a few hours into a gelatinous mass. The same result is achieved if we replace the carbonate of baryta by an alcoholic solution of ethylate of baryta until the solution is neutral. This gelatinous mass is thrown on a filter, washed with absolute alcohol, and dried on a porous plate in the presence of caustic potash.

We thus obtain a white salt soluble in water, which, after desiccation in the hot-air oven at a temperature of from 110° to 120°, gives on analysis a composition corresponding to the formula $C_6H_2P_8O_{20}Ba_2$. The results of the analysis are—

	Calculated.	Found. I.	II.	III.	IV.	V.
C	7·86	8·02	7·95	—	—	—
H	0·21	0·36	0·28	—	—	—
P	27·07	—	—	27·67	26·86	—
Ba	29·92	—	—	—	—	30·57

The acid of this salt should be $C_7H_2P_8O_{20}H_4$; it should result from the union of one molecule of benzene with four molecules of phosphoric anhydride ($C_6H_6+4P_2O_5$).

Its constitution may be explained by the following graphic formula:—



This should thus be *benzenetetradimetaphosphoric acid.*

I propose to study the properties of this acid and its salts in detail, and to try and isolate various combinations—which theory enables me to predict—formed by the union of the anhydride or of the phosphoric acids with benzene or with other organic compounds of the same order.—*Comptes Rendus*, cxxvi., No. 8.

SODIUM PEROXIDE IN QUANTITATIVE ANALYSIS.*

By C. GLASER.

W. Hempel (*Ztschr. Anorg. Chem.*, 1892, iii., 193-194) and J. Clark (*J. Chem. Soc.*, 1893, 1079) first proposed to use sodium peroxide in quantitative analysis. Hempel employed it for the oxidation of chromium, manganese, tungsten, and tin, and subsequent determination by known means; he also mentions that sulphur is completely oxidised to trioxide. He further recommends the reagent for the decomposition of zinc-blende and galena.

J. Clark recommends it for the estimation of sulphur, arsenic, and chromium, also for the separation of manganese from zinc, nickel, and cobalt. He states (*Ibid.*, lxiii., 1079) that the action of sodium peroxide on coke and coal is too violent for analytical purposes. T. Spüller and S. Kalman (*Chem. Ztg.*, xvii., 18) use it on ferrochrome, chrome steel, chrome iron, and also sulphurets. Poleck (*Chem. Ztg.*, xviii., 103) experimented on organic substances, as did J. Tafel (*Ber. d. Chem. Ges.*, xxvii., 816).

In 1894 M. Hoehnel and C. Glaser (*Arch. Pharm.*, ccxxxii., 222; *Chem. Ztg.*, xviii., 1148) made revised recommendations for the estimation of sulphur in pyrites. O. Kassner (*Arch. Pharm.*, ccxxxii., 226) states that iron is precipitated as hydroxide, but not changed into ferric acid,—that, on the contrary, solutions of ferric acid are reduced by sodium peroxide. He gives detailed statements concerning separation of chromium and manganese; of the decomposition of freshly precipitated sulphides of antimony, tin, and arsenic. In 1895, L. Archbutt (*Analyst*, xx.) reports an analysis of sodium

* A review of various propositions made since 1892.

peroxide, showing the presence of nearly one-half of 1 per cent of iron and alumina in the commercial article. Alb. Edinger (*Ztschr. Anal. Chem.*, xxxiv., 362) gives his experience in the determination of sulphur and chlorine in inorganic and organic combinations. M. C. Schuyler (*Chem. Ztg.*, xx., 1896) proposed to determine mercury in mercuric salts by reduction to metal with sodium peroxide. In 1897 S. W. Parr (*J. Am. Chem. Soc.*, xix., 341) reports on the adaptability of sodium peroxide as a third group reagent in qualitative analysis, practically a review of the above-named publications, omitting quantitative features.

The *Chemiker Zeitung* (*Chem. Ztg.*, xxi., No. 6) contains a second note of the author, suggesting some improvements in the determination of sulphur in pyrites, and later the same author (*Ibid.*, xxi., No. 69) separated iron from aluminum in phosphates and other minerals by means of sodium peroxide.

It may be in place here to state that the C.P. sodium peroxide of the trade has, as far as I have had occasion to test it, proved quite free from oxide of iron and alumina. It appears therefore probable that the article analysed by Archbutt was a crude commercial product.

I cannot confirm O. Kassner's statement that iron is not oxidised to ferric acid by sodium peroxide. If the reagent is added to a solution of an iron salt, without the precaution of keeping the temperature of the latter sufficiently low, his statement holds good. But if this last condition is complied with by keeping the solution comparatively cool, a sufficient excess of the reagent will produce a perfect solution, as I have stated in the above last-named paper.

I desire especially to recur to J. Clark's statement that the action of sodium peroxide on coke and coal is too violent to permit of use in analysis. I have used this reagent in a considerable number of coke, coal, and asphalte analyses for sulphur with perfect success, and I now present a short description of the method as I carry it out.

The material to be analysed is placed in a sufficiently large silver or nickel dish, and covered with about four times its weight of sodium carbonate. Upon this a piece of sodium hydroxide is laid, about one-half the weight of the carbonate used.

The dish is now moved carefully and slowly over a small flame until the gas generation subsides and a half-fused mass is obtained. Upon this mass dry sodium peroxide is now dusted from a porcelain or platinum spoon in small quantities at a time, always waiting until the reaction is over. This is continued until all carbon is burned away, when the mass, if necessary, is heated to perfect fusion. Usually this is obtained by the heat generated by the combustion in the dish, which, however, takes place so quietly that no loss by explosion or spurting will occur. After this operation the determination of sulphur is carried to an end in the well-known way.

I believe that this method will prove quite a relief to those chemists who have to make many sulphur determinations in coke and coal, and who know the uncertain working of a fusion with potassium nitrate. At least it has been my experience that it is difficult to so regulate the temperature of the fusion as to avoid explosion with loss. Even the use of double crucibles has not always proved successful. The time required for the operation with sodium peroxide is quite short; with coke about five minutes, with coal probably ten, while with asphalte —owing to the peculiar nature of the material—it will take a little longer.

In analysis of chrome ores, sodium peroxide does not appear to fulfil the hopes of those chemists who first proposed it. The oxidation is reported to be never perfect in one operation, which makes the method more complicated and troublesome than a fusion with potassium nitrate and borax.

This was to be expected, since even chromic salts in solution require more than one treatment with sodium peroxide before complete oxidation to chromic acid is effected.

With this exception sodium peroxide has proved a very useful and convenient reagent, applicable in a great number and variety of cases. It ought to be, and no doubt will become, one of the standard reagents of a modern laboratory.—*Journal of the American Chemical Society*, xx., No. 2, 1898.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 3rd, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

MR. CECIL J. BROOKES was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Joseph Btierley, B.Sc., Ashton Road, Failsworth, Manchester; Arthur William Cowburn, Fernroyd, Bowdon, Cheshire; Charles Benjamin Dudley, Ph.D., Attoona, Penn., U.S.A.; Arthur Leonard Harry Garside, c/o C. Lawes and Co., Barking Creek; Lawrence Hislop, Gas Works, Uddingston; F. Hurter, Ph.D., Holly Lodge, Cressington Park, Liverpool; Samuel Morton Jessop, 12, Hanson Terrace, Wakefield; George Henry Masson, M.D., M.S., 22, Lauriston Place, Edinburgh; Walter Charles Cross Peters, 14, Trinity Square, S.E.; Francis Pitt Smith, B.Ph., 77, Woodland Avenue, New Rochelle, N.Y., U.S.A.; Thomas de Smith, B.A., Eastbourne College, Eastbourne; William Thomas Newton Spivey, M.A., 5, Trumpington Street, Cambridge; John Alexander Williamson, 81, Cheverton Road, Upper Holloway, N.; Thomas Barlow Wood, M.A., Caius College, Cambridge.

Of the following papers those marked * were read:—

*24. "*Preparation of Anhydrous Hydrogen Cyanide and Carbon Monoxide.*" By JOHN WADE, B.Sc., and LAURENCE C. PANTING, M.B.

On allowing a cold mixture of equal volumes of sulphuric acid and water to drop on to 98 per cent "lump" potassium cyanide, hydrogen cyanide, accompanied by traces of water only, is evolved in almost theoretical amount, and with the aid of suitable condensing apparatus is readily collected in quantity. With concentrated sulphuric acid, on the other hand, but still at the ordinary temperature, nearly pure carbon monoxide is evolved, also in quantity approaching the theoretical; provided certain precautions are taken, it is free from dioxide, and is accompanied only by small quantities of hydrogen cyanide.

In discussing the mechanism of the formation of the monoxide, experiments are described showing that part of the water required for the hydrolysis is derived either from the sulphuric acid itself or from the potassium hydrogen sulphate formed in the course of the action, and that consequently the sulphuric acid acts at the same instant both as a hydrolyst and as a dehydrating agent.

*25. "*Production of some Nitro- and Amido-oxylutidines.*" By J. N. COLLIE, Ph.D., F.R.S., and THOMAS TICKLE.

In a former paper (*Trans.*, 1897, lxxi., 838) one of the authors drew attention to the fact that various nitro- and amido-derivatives of pyridine could be obtained by the ordinary process of nitration and reduction of certain oxypyridine compounds. These substances correspond in the pyridine series to nitro- and amido-phenols in the benzene series, and as some of the reactions (especially those with various oxidising agents) of the amido-oxy-

pyridines resemble those of alkaloids, the investigation has been continued.

Pseudolutidostyril ($\alpha\gamma$-dimethyl-α'-oxypyridine) gave on nitration a *nitropseudolutidostyril*, $C_5HNMe_2(OH)NO_2$. It crystallises in light yellow needles that melt with much decomposition at about 250°. The hydroxyl- and nitro-groups are in the ortho-position to one another, but the substance is not volatile with steam. With alkalis, it forms brilliant yellow compounds.

When the nitro-compound is reduced with tin and hydrochloric acid, an amidopseudolutidostyril is produced. The hydrochloride of this base, $C_5HNMe_2(OH)NH_2HCl$, crystallises in needles which decompose without melting at 235—240°. By the action of sodium bicarbonate, the free base can be obtained in the form of a bulky mass of fine needles, m. p. 205° corr.). The base is very soluble in hot water, but much less so in cold. It oxidises readily, and an aqueous solution on boiling turns brown. This solution reduces silver nitrate at once. With ferric chloride it gives first a red and then a bright green colour, and when dissolved in strong sulphuric acid, if a drop of fuming nitric acid be added, a brilliant purple colour is momentarily produced. It forms a platinichloride and an acetyl derivative, m. p. 255° (corr.).

By nitrating ethylic pseudolutidostyrilcarboxylate (m. p. 137—138°) a nitro-derivative was formed, $C_5N{\cdot}Me_2(OH)(CO_2Et)NO_2$. This substance, m. p. 215° (corr.), crystallises in yellow needles. On hydrolysis, it yielded the corresponding acid, m. p. 260° (corr.), which when pure is almost colourless, but forms bright yellow salts. The acid on heating loses carbon dioxide and the same nitro-pseudolutidostyril (m. p. about 250°) was obtained.

Amido-pseudolutidostyrilcarboxylic acid was prepared from the corresponding nitro-acid by reduction. Its hydrochloride crystallises from water in needles with two molecules of water. The amido-acid melts at 275° (corr.), and contains one molecule of water of crystallisation; above its melting-point it decomposes, yielding amido-pseudolutidostyril (m. p. 205° corr.). Its salts reduce silver nitrate solution, and with ferric chloride give a green colouration.

*26. "*Production of some Nitro- and Amido-oxylutidines.*" (Part II.). By Miss L. Hall and J. Norman Collie, Ph.D., F.R.S.

Lutidone, $\alpha\alpha'$-dimethyl-γ-oxypyridine, when warmed with nitric acid, does not yield a nitro-derivative (*Trans.*, 1897, lxxi., 838) but a nitrate of lutidone. If, however, a mixture of strong nitric and sulphuric acids are employed, the nitro-compound is formed, $C_7H_9NO + HNO_3 = C_7H_8NO{\cdot}NO_2 + H_2O$. This nitro-lutidone is a pale yellow crystalline compound, possessing a strong acid reaction, and dissolving in alkalis with an intense yellow colour; it is not volatile in steam. When reduced with tin and hydrochloric acid, it yields an amido-lutidone, $C_7H_8NO{\cdot}NO_2 + 3H_2 = C_7H_8NONH_2 + 2H_2O$. This amidolutidone, unlike amidodioxypicoline and amidopseudolutidostyril, does not give characteristic colours with oxidising agents, but acts as a strong reducing agent. It forms both a monohydrochloride and a dihydrochloride. The platinichloride is unstable; it undergoes reduction when dissolved in water and warmed, but if its hydrochloric acid solution is boiled, a very insoluble platinichloride separates, which seems to be the salt of propine diamine,—

$$\begin{matrix} Me{\cdot}C{\cdot}NH_2 \\ \| \\ HC{\cdot}NH_2 \end{matrix} \quad 2HCl{\cdot}PtCl_4,$$

the decomposition having been brought about by hydrolysis, $C_7H_{10}N_2O + 3H_2O = C_3H_8N_2 + 2C_2H_4O_2$. This breaking down of the pyridine ring is of considerable interest, and, in a substance like lutidone, is hardly to be expected, since the nitrogen atom is bound to two carbon atoms, neither of which are united to oxygen, and, moreover, lutidine is not the anhydride of an amido-acid.

Discussion.

Mr. Ling pointed out that certain anilides give, when treated with oxidising agents in acid solution, colour reactions similar to those obtained with alkaloids (Tafel, *Ber.*, 1892, xxv., 412; Schär, *Archiv. Pharm.*, 1894, ccxxxii., 249).

Prof. Collie, in reply to suggestions of Dr. Wynne, pointed out that it was impossible in the case of lutidone to obtain more than one mono-nitro-derivative. In nitrating pseudolutidostyril, the position of the entering nitro-group had been determined with certainty by the fact that pseudolutidostyrilcarboxylic acid, after nitration and subsequent heating, yielded the same nitro-compound as had been obtained from pseudolutidostyril itself.

*27. "*On Benzene Hexabromide.*" By F. E. Matthews, Ph.D.

In this paper, the author describes his failure to isolate the second modification of benzene-hexabromide, obtained, in minute quantity, by Orndorf and Howells (*Amer. Chem. Journ.*, 1896, xviii., 312—319) even from considerable quantities of the crude hexabromide; also the failure to prepare either the hexachloride or hexabromide of bromobenzene; in the former case owing to the displacement of chlorine by bromine, and in the latter to the substitution of bromine taking place more readily than direct addition.

The action of alcoholic soda upon benzene hexabromide is also described, the product of the action being a mixture of paradibromo- and tribromobenzene (1 : 2 : 4), possibly mixed with a small amount of one of the other dibromobenzenes. Benzene obtained from the hexabromide by nascent hydrogen in acid alcoholic solution yields both modifications of the hexachloride on treatment with chlorine.

Discussion.

Professor Tilden was glad that Dr. Matthews had resumed work on these interesting compounds. He had repeated some of Dr. Matthews's experiments, and had satisfied himself that the hexachloride was obtainable very readily and in very large proportion. It was somewhat remarkable that the corresponding bromide should be formed so much less readily.

Dr. Matthews stated that he had always worked with material spontaneously precipitated from the mixture of benzene, bromine, and water, and not with the substance left after evaporating the mixture to dryness, as was the case with Orndorf and Howells.

*28. "*Note on the Action of Bromine on Benzene.*" By J. Norman Collie, Ph.D., F.R.S., and Colin C. Frye.

The authors have repeated the work of Ador and Rilliet (*Ber.*, 1875, viii., 1286), who stated that when bromine was allowed to act on excess of benzene in sunlight, dibromo-addition products were produced, which, after treatment with zinc ethyl and subsequent oxidation with chromic acid, yielded metabromo- and metaphthalic-acids, together with benzoic acid, parabromobenzoic and terephthalic acid, but they were unable to obtain any ortho-compounds. The authors have succeeded in proving the presence of ortho-compounds, and at the same time have confirmed the observations of Ador and Rilliet, having isolated para-bromobenzoic acid and metaphthalic acid.

Discussion.

Dr. Matthews said that he had made several attempts to isolate di- and tetra-chlorine and bromine addition-compounds of benzene, both by the action of the halogens upon excess of benzene and also by decomposition of the hexabromide and hexachlorides of benzene, but always without finding a trace of any di- or tetra-halogen addition-derivative.

*29. "*Note on Manganic Salts.*" By C. E. Rice, B.A.

The author shows that the decomposition of manganic chloride in solution into manganous chloride and chlorine is reversible, the velocity of the reverse change being very small. He also describes the production and analysis of two double manganic chlorides, $2KCl{\cdot}MnCl_3{,}H_2O$ and

$2NH_4Cl{\cdot}MnCl_3{,}H_2O$, but obtains no evidence of the existence of any compound of the formula $MnCl_4$.

DISCUSSION.

Professor CLOWES asked which of the manganese hydroxides was precipitated by the action of water upon the crystalline hydrated double chloride; it would be interesting to know whether a hydroxide corresponding to the formula $MnCl_3$ could exist.

Professor TILDEN remarked that the manganese tetrachloride seemed to be now finally disposed of, and in representing the production of chlorine by the usual process we should have to write a new equation.

Mr. RICE, in reply, said that he had not considered it necessary to investigate the point, since Pickering had shown that when the solution obtained by dissolving any of the higher oxides of manganese (Mn_2O_3, Mn_3O_4, MnO_2) in hydrochloric acid is diluted, the precipitate consists of a mixture of these hydrated oxides in varying proportions.

*30. "*Some Chemical Properties of Concentrated Solutions of certain Salts.* Part I. *Potassium Carbonate.*" By W. COLEBROOK REYNOLDS.

When the salts of certain other metals are added to a concentrated solution of potassium carbonate, double salts are formed which are sometimes, as in the case of iron, copper, nickel, and cobalt, soluble in the solution, instead of the normal or basic carbonates which are formed when a dilute solution is employed.

These double salts and their solutions are decomposed by pure water. To obtain them, the chloride, nitrate, or preferably the acetate, is added to a concentrated solution of potassium carbonate (sp. gr. 1·55), and the liquid left to crystallise. The author has isolated the following double salts in well-defined crystalline form:—$CuK_2(CO_3)_2$, $CuK_2(CO_3)_2{,}H_2O$, $CuK_2(CO_3)_2{,}4H_2O$, $MnK_2(CO_3)_2{,}4H_2O$, $FeK_2(CO_3)_2{.}4H_2O$, $CaK_2(CO_3)_2$, $Bi_2OK_4(CO_3)_4\,H_2O$, $CoK_2(CO_3)_2{.}4H_2O$, $NiK_2(CO_3)_2{,}4H_2O$, $MgK_2(CO_3)_2{,}4H_2O$, $AgKCO_3$. The last four salts have been previously obtained by other chemists.

DISCUSSION.

Professor TILDEN said that Mr. Reynolds had been led to the study of these compounds in the course of enquiring into the production of the recently discovered percarbonates. In dilute solution, potassium carbonate appeared to be resolvable into the ions 2K and CO_3, while in a saturated solution it behaved as though made up of K and KCO_3. Mr. Reynolds had omitted to point out that in the formulæ of all his new double carbonates, the heavy metal seemed to be associated with a proportion of KCO_3 corresponding to its valency. Perhaps this was only a coincidence, but it seemed to deserve notice.

Mr. A. G. BLOXAM remarked that if carbonic acid was regarded as a hydroxy-acid, the formation of a deep blue coloured solution by mixing a concentrated solution of potassium carbonate with a solution of copper sulphate became of interest as bringing carbonic acid into line with other hydroxy-acids, all, or nearly all, of which were known to give deep blue coloured solutions with copper sulphate and alkali sufficient to satisfy both the acidic and phenolic or alcoholic hydroxyl groups. Such solutions, however, were more stable than the potassium-copper carbonate solution of Mr. Reynolds, and this might be due to a comparatively unstable condition of potassium carbonate in solution; if a strong solution of this salt was partly decomposed on dilution, potassium hydroxide and bicarbonate being formed, a corresponding decomposition of the copper compound would be expected. He would be glad to learn from Mr. Reynolds whether addition of potassium hydroxide hindered the precipitation of copper carbonate on dilution.

Mr. W. P. BLOXAM asked whether the formation of these salts was attended with the evolution of carbon dioxide. Had the author taken into account the hydrolysis of potassium carbonate which took place in aqueous solution? According to a paper published by Senderens, the action of a non-metallic element (sulphur) upon solution of potassium carbonate could be explained by regarding the salt as hydrolysed thus, $H_2O+K_2CO_3=KHCO_3+KOH$; and experiments made by the speaker showed that even a concentrated solution of the salt must be regarded as possessing this constitution. The presence of more oxygen in the double carbonate of bismuth than that present in the acid groups would be explained by the action of the hydroxide groups present in the carbonate solution. The same reaction would also explain the difficulty of obtaining manganous and ferrous double carbonates.

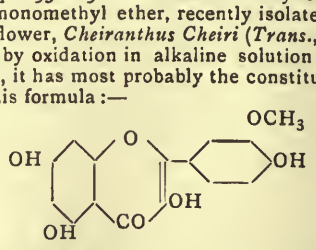
Mr. REYNOLDS, in reply, stated that it was possible to represent the formation of these compounds as taking place in accordance with such an equation as, for instance, $MnCl_2+2K{\cdot}KCO_3=Mn(KCO_3)_2+2KCl$, and this view was strengthened by the fact that some of the salts, as, for instance, copper acetate, dissolved immediately without forming a precipitate which subsequently re-dissolved.

In the case of the double succinates, however, where exactly the same phenomena occurred, the composition of the copper compound was $CuK_4(C_4H_4O_4)_3{,}2H_2O$, and this could not be represented by a similar equation. He had, therefore, not introduced such views into the present paper, as they did not appear to be generally applicable.

The author did not think that any of the phenomena supported the view that the solution contained potassium hydroxide and potassium bicarbonate, as no effervescence occurred, except in the case of normal bismuth salts, when basic salts were formed.

31. "*The Colouring Matters of the Indian Dyestuff Delphinium zalil.*" By A. G. PERKIN and J. A. PILGRIM.

"Asbarg" consists of the dried flowers and flowering stems of the *Delphinium zalil*, found in great quantity in Afghanistan, and which is much used in India for the production of a yellow colour on alum mordanted fabrics. The flowering stems are nearly devoid of dyeing property. For the supply of material we are indebted to the authorities of the Imperial Institute. Three colouring matters exist in this plant in the form of glucosides. The sparingly soluble colouring matter, $C_{16}H_{12}O_7$, forms glistening yellow needles, soluble in alkalis with a yellow colour. Fused with alkali it yielded phloroglucinol and protocatechuic acid, and by means of hydriodic acid it yielded quercetin with the evolution of 1 mol. of methylic iodide. By methylation it was converted into quercetin-tetramethyl ether, and by acetylation into a tetracetyl derivative of the formula $C_{16}H_8O_7(C_2H_3O)_4$, colourless needles, m. p. 195—196°. It was evidently *isorhamnetin*, a quercetinmonomethyl ether, recently isolated from the yellow wallflower, *Cheiranthus Cheiri* (*Trans.*, 1896, lxix., 1650). As by oxidation in alkaline solution this yields vanillic acid, it has most probably the constitution represented by this formula:—



With alumina as mordant it dyes a purer yellow than quercetin. The chief constituent of the more soluble portion was recognised to be identical with *quercetin*, the colouring matter of quercitron bark. The residual colouring matter, present only in small quantity, was not obtained in a pure condition. It resembled quercetin in percentage composition, and in its decomposition products, but differed from it in not reacting with alcoholic potassium acetate, and the melting-point of its acetyl derivative. "Asbarg" resembles quercitron bark in dyeing property, but has only 35 per cent the tinctorial power of this dye-stuff. It contains, when freed from the flowering stalks, 3·47 per cent of colouring matter (not as glucoside).

32. "*Some Metallic Salts of Natural Yellow Colouring Matters.*" By A. G. PERKIN and P. J. WOOD.

That certain colouring matters decompose alkaline carbonates with the formation of acid salts has been previously demonstrated. Thus of morin, Hlasiwetz and Pfaundler describe salts of this description, and of quercetin (*Jahresbericht*, 1864, 560). Further, from gentisin, Hlasiwetz and Habermann (*A.*, 1875, clxxv., 73) obtained analogous compounds. Among other instances is bixin, the colouring matter of annatto, which Etti describes (*Ber.*, 1878, xi., 864) as giving a sodium and a potassium salt, and rottlerin, from which one of us obtained similar compounds (*Trans.*, 1895, lxvii., 230).

Owing probably to the formation of acid salts these alcoholic alkaline solutions are not readily neutralised completely by acetic acid, and as it appeared that some of the formulæ of the above compounds must be incorrect, this reaction was studied. It was found that in alcoholic solution, quercetin, morin, fisetin, and myricetin decompose potassium and sodium acetates with the formation of sparingly soluble salts. *Potassium quercetin*, $C_{15}H_9O_7K$ (found, K = 11·46; theory requires K = 11·47), forms minute orange-yellow prismatic needles, insoluble in cold water, and but slowly decomposed by boiling dilute acetic acid. *Sodium quercetin*, $C_{15}H_9O_7Na$, closely resembles the above salt. *Potassium morin*, $C_{15}H_9O_7{\cdot}K$ (found, K = 11·97; theory requires K = 11·47), separates as glistening orange-coloured needles, and is closely resembled by *sodium morin*, $C_{15}H_9O_7Na$ (found, Na = 6·89; theory, 7·09). Morin reacts with magnesium and ammonium acetates, though from quercetin salts have not been obtained in this way. *Ammonium morin* and *magnesium morin* separate in the form of long needles in a similar way (found, Mg = 3·52; theory requires Mg = 3·83 per cent).

Fisetin and myricetin apparently yield analogous derivatives, and on the other hand luteolin, apigenin, chrysin, and gentisin do not appear to react with alkaline acetates. With the exception of bixin and rottlerin, as yet but little examined, the above colouring matters are known to contain no carboxyl group, and it is thus of interest to study this reaction in which only one of the numerous hydroxyls present takes part. It appears probable that some analogy exists between these salts and the acid compounds of the colouring matters described by one of us (*Trans.*, 1896, 69, 1439).

33, "*The Interaction of Magnesium and Solution of Copper Sulphate.*" By Edward Divers, M.D., F.R.S.

Neither Clowes and Caven nor Tilden, in their communications made to the Society in November last, seem to the writer to have recognised the significance of the results of the interaction of magnesium metal and a solution of copper sulphate. Remarkable as these results are, it is to be remembered that a closely analogous case had long been known, even when Commaille in 1866 observed them, namely, that of zinc immersed in a solution of an alum. Here, also, there is free evolution of hydrogen and precipitation of basic sulphate, and, when chromium alum replaces the aluminium salt, there is also reduction of some of the chromic sulphate to chromous sulphate. The only part of the change which finds no parallel in the action of zinc upon chrome alum is that of the deposition of a little copper, but this deposition is quite in accordance with the general behaviour of copper salts.

The formation of basic salt and hydrogen is a change independent of that of reduction, as is clearly shown by the same formation taking place, without that of reduction, when aluminium sulphate or common alum is concerned. Now, since the alum solution is dialysable into sulphuric acid and basic aluminium or chromium sulphate (besides potassium sulphate), and is also strongly acid in reaction, it will be admitted by all that the action in the case of an alum is really that of dilute sulphuric acid upon the zinc. The gradual precipitation of the previously soluble basic salt as the zinc dissolves in the solution is just what happens when zinc sulphate is dissolved in a dialysed solution of aluminium, or chromium hydroxide, or basic sulphate. These two points being admitted, it will be very difficult to doubt that similar changes occur between copper sulphate and magnesium, or, in a less degree, zinc; for the solution is here also very acid in reaction and needs only a little boiling to make it deposit basic sulphate; besides, too, it will unquestionably show largely that hydrolysing action upon cane-sugar which Long (*J. Amer. Chem. Soc.*, 1896, 18, 120) has recently shown so many metallic salts possess, and this property is evidence that, like aluminium sulphate, it is partly hydrolysed into sulphuric acid and soluble basic sulphate, which will be precipitated as magnesium goes into the solution. Caven and Clowes have pointed out the inadequacy of the action of the magnesium-copper couple to account for the large evolution of hydrogen. Their unsupported suggestion that the hydrogen is formed by the combined action of copper sulphate (as such) and magnesium upon water, has likewise little claim to consideration in presence of the fact that hydrolysed aluminium sulphate acts in the same way as copper sulphate.

Coming now to the production of cuprous oxide, a separate reaction, or set of reactions, there would be nothing in this unlike that of the reduction of ferric or chromic sulphate by zinc or magnesium, could cuprous salt only be found in solution. When, in place of the sulphate, cupric chloride is used, then, as everyone knows, there is just this looked-for reduction to cuprous salt. But the peculiarity of copper is that oxylic cuprous salts are apparently unable to exist. It is, however, not so improbable that in dilute solution and in presence of much cupric sulphate a little cuprous sulphate may exist for a very short time. According, indeed, to Rose, from roasted copper sulphide water extracts, along with cupric sulphate, a little cuprous sulphate, which then gradually decomposes into metal and cupric salt, just as a mercurous salt in water will change into metal and mercuric salt (*Annalen*, 1841, 39, 109). However that may be, and the observation admits of another interpretation, it does seem to the writer that the precipitation of cuprous oxide during the action of magnesium upon cuprous sulphate is a fact highly favourable to the view that cuprous sulphate is actually formed, part of it then quickly decomposing into cupric sulphate and metallic copper, and the rest of it being decomposed by the basic cupric salt into normal cupric sulphate and cuprous oxide. With certainty he can state that, when finely divided copper is acted upon by nitrogen peroxide, nitric oxide and a copper nitrate are formed, and no nitrite, and that this copper nitrate, when touched with water, decomposes into cupric nitrate and bright metallic copper, thus proving, apparently, that in absence of water cuprous nitrate can exist, and, therefore, by analogy, other oxylic cuprous salts.

There remains only to notice Tilden's suggestion that some of the hydrogen reduces cupric to cuprous oxide. Hydrogen is known not to have such an action, and therefore the usual assumption of there being a more active "nascent" hydrogen has to be made, but also without the least foundation in experience. In the present case, it may be pointed out, firstly, that in the reduction of chromic sulphate to chromous sulphate by zinc, hydrogen continues to be evolved, although very great excess of chromic salt is always in contact with the zinc; and, secondly, that in the reduction of ferric salts by zinc it has been established that this takes place much more rapidly when clean zinc dust is put into the ferric solution in the absence of excess of acid, than when, as is usual, an excess of acid is added to generate hydrogen. It may, therefore, with great probability be assumed that the reactions are $2CuSO_4 + Mg = Cu_2SO_4 + MgSO_4$ and $Fe_2(SO_4)_3 + Zn = 2FeSO_4 + ZnSO_4$, hydrogen having nothing to do in the matter.

PHYSICAL SOCIETY.

Ordinary Meeting, March 11th, 1898.

Mr. Shelford Bidwell, President, in the Chair.

Prof. J. D. Everett gave a communication on "*Dynamical Illustrations of certain Optical Phenomena.*"

The first part of the paper deals with the properties of a series of equal particles attached at equal intervals to an uniform stretched elastic weightless string. Their free simple-harmonic modes of wave-motion are first investigated. The highest frequency occurs when the wave-length is double that of the common distance a. As the wave-length increases from $2a$ to infinity, or diminishes from $2a$ to a, the frequency tends to zero. To every wave-length λ_1 between $2a$ and infinity, there corresponds a wave-length λ_2 between $2a$ and a, such that—

$$\frac{a}{\lambda_1}+\frac{a}{\lambda_2}=1.$$

The frequency is the same for λ_2 as for λ_1. Further examination shows that the difference of wave-length between these two solutions is only apparent, and that, so far as the movements of the particles are concerned, waves of length λ_1 travelling in one direction, are identical with waves of length λ_2 travelling in the opposite direction. The same is true if $a/\lambda_1 + a/\lambda_2$, instead of being unity, is equal to any integer. On the other hand, if the difference between a/λ_1 and a/λ_2 is an integer, the two sets of waves travel in the same direction. Any simple-harmonic wave-motion of the system of particles may thus be regarded as having any one of an infinite number of wave-lengths. When one particle of the system is constrained to a S.H. motion, of frequency not exceeding that which corresponds to $\lambda=2a$, the whole system will ultimately vibrate in equal waves. When the frequency of the constrained particle exceeds that due to $\lambda=2a$, the ultimate state will be S.H. motion with exact opposition of phase between successive particles. The simultaneous displacements of the particles at any instant, as we travel away from the constrained particle in either direction, form a diminishing geometrical progression, with signs alternately plus and minus. Expressions are investigated for the constraining force, and for the ratio of the energy of the system (consisting of an unlimited number of particles) to the energy of the constrained particle.

The second part of the paper deals with pendulums. (1.) Sympathetic pendulums, such as two equal pendulums suspended from the same support. (2.) Double pendulums, *i. e.*, one simple pendulum suspended from another. In each case the investigation consists in seeking a mode of vibration in which the two bobs have either identical or opposite phases, so that their displacements are in a constant ratio, positive or negative. In every case there are two such modes, one with a positive and the other with a negative ratio. As regards the sympathetic pendulums:—When they are equal in mass and length the periods for the two modes are approximately equal, and the displacement of each pendulum follows the law of a "curve of beats"; the excursions are largest for one pendulum when they are smallest for the other. As regards the double pendulum:—When the lower mass is much less than the upper there exist, in like manner, motions following the law of beats, provided that, to start with, one bob is at rest in the zero position, and the other at rest in an extreme position. If the lengths of the two strings are decidedly unequal, one fundamental mode has approximately the period of the upper, and the other the period of the lower pendulum. In the former, the displacements of the two bobs are comparable; in the latter, the displacement of the upper is small compared with the lower. The bearing of these conclusions is pointed out, first, on Lord Kelvin's conclusions respecting a suspended clock; and, secondly, on Lord Rayleigh's assertion (frequently quoted in connection with anomalous dispersion) respecting the influence on a heavy pendulum of a much lighter one suspended from it. To obtain the phenomenon of beats in perfection the upper string must be slightly longer than the lower, and the ratio of difference to sum of lengths must equal the ratio of lower mass to upper. The beats thus obtained explain the experiment described in the second edition of "Rayleigh on Sound," § 62. Sellmeier's application of the beats of double pendulums to explain fluorescence is briefly described. Stokes explains fluorescence by the analogy of the chain of equal particles discussed in the first part of the paper. Forced vibrations quicker than the critical frequency are produced by the action of the vibrating ether on the fluorescent body; and when the body is left to itself its subsequent motion is made up of S.H. components, all of which are below the critical frequency.

Prof. R. A. Lehfeldt then read a paper on "*The Properties of Liquid Mixtures.*"

In a previous communication (*Phil. Mag.*, [5], vol. xl., p. 398) the author follows out the consequences of a certain thermo-dynamic relation between the composition of a liquid mixture and that of the vapour in equilibrium with it, and the saturation-pressure of the system. More stable compounds are now chosen, viz., benzene and toluene mixed with carbon tetrachloride, as types of normal organic compounds; and benzene and toluene mixed with ethyl alcohol as types of a so-called "associated liquid."

These experiments have been carried out in the Davy-Faraday Laboratory.

The measurements come under two distinct groups:—(1) Vapour-pressure; (2) composition of vapour. They were made separately, on material from the same source, prepared identically. To measure the vapour-pressure of the mixtures the "dynamic" method was adopted. An experiment consists in weighing out a mixture, taking its refractive-index by a Pulfrich refractometer, placing it in a boiling tube, and, after adjusting temperature and pressure, taking observations at different temperatures on a rising scale, and then on a falling scale. The refractive index of the residue is again measured; this is always used for checking the composition of the mixtures. For determining the composition of the vapour over liquid mixtures, the method used is to distil a little of the mixture and analyse the distillate. The apparatus is arranged so that the distillate can be drawn off by a tap as required.

The author criticises the results of Linebarger (*Journ. Amer. Chem. Soc.*, vol. xvii.), and also those of Margules (*Wein. Ber.*, vol. civ.). Linebarger states that the partial pressure of benzene and toluene in mixtures is simply proportional to the molecular percentage present. This conclusion, the author considers, is only roughly true; the partial pressure of the hydrocarbon vapour is not necessarily linear in mixture. Hence, the rule proposed by Linebarger for determining the molecular weight is incorrect.

The President proposed votes of thanks to the authors, and the meeting was adjourned until March 25.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

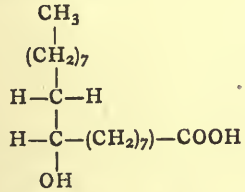
Journal fur Praktische Chemie,
No. 1, 1898.

Chlorine and Bromine Derivatives of β-Naphthylamines,—Ad. Claus and O. Jäck.—This paper contains a

description and properties of a large quantity of chlor- and brom-derivatives of β naphthylamines.

The Liquid Fatty Acids of the Fat of Dogfish.—Eugen Ljubarsky.—The fat of the Caspian dogfish was found to be a reddish liquid with a disagreeable fatty smell. If it was left in a vessel open to the air it became covered with a skin, darker in colour and smelling very bad. This fat when examined was found to consist of 17 per cent of saturated acid, in all probability palmitic acid. The remaining 83 per cent consisted of oleic acid, $C_{18}H_{34}O_2$, and physeloleic acid, $C_{16}H_{30}O_2$.

Action of Sulphuric Acid on Elaïdic Acid.—Alex. Tscherbakoff and A. Saytzeff.—A theory is put forward that oleic and elaïdic acids are stereo-isomers. In confirmation of this it is found that by treatment with sulphuric acid and potash both yield the same oxystearic acid, having the constitution—



Theoretically oleic and elaïdic acids should yield two different oxystearic acids, related as racemic and meso-tartaric acid, but it is suggested that in oxystearic acid one form only is stable.

The Trivalent Alcohol of Allyldipropylcarbinol.—Alexis Bogorodsky.—This substance was prepared by the action of a dilute solution of potassinm permanganate on allyldipropylcarbinol, the permanganate solution heing added in small quantities and kept cool. The glycerin was extracted with ether and dried in a vacuum desiccator. It was shown to have the constitution—

$$\begin{matrix} C_3H_7 \\ C_3H_7 \end{matrix}\!\!>\!C.OH-CH_2-CH.OH-CH_2OH.$$

An attempt to prepare the acetic ether of the glycerin by heating the glycerin with acetic anhydride in sealed tubes was unsuccessful; apparently some quantity of diacetyl-ether derivative was formed.

Methyldiethylethylene.—Mich. Saytzeff, jun.—This substance was prepared by distilling a mixture of triethylcarbinol—

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!C\!<\!\begin{matrix} C_2H_5 \\ OH \end{matrix}$$

and oxalic acid. It boils at 97°—98° and has a specific gravity of 0·72544 at 15°. It has the constitution—

$$(C_2H_5)_2C = C.H.CH_3.$$

An attempt to oxidise it with potassium permanganate to the corresponding glycoll gave only negative results, fatty acids of low molecular weight being the chief products.

Allylethylphenylcarbinol. — Al. Bogorodsky and J. Ljubarsky.—The method employed for the preparation of this substance was the action of allyliodide and zinc upon ethylphenylketone. The liquids were dropped from a dropping-funnel upon finely-powdered well-etched zinc. The oily product was separated from the water, dried over melted potash, and then distilled. The purest fraction obtained had a boiling-point of 238—242°. It was a mobile highly refractive liquid, insoluole in water and of lower specific gravity. An attempt was made to transform it into the corresponding glycerol by means of potassium permanganate (dilute). This succeeded, and a very thick syrup was obtained which gave on analysis numbers corresponding to those calculated for the formula—

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!C.OH-C_3H_5(OH)_2.$$

MEETINGS FOR THE WEEK.

Monday, 21st.—Society of Arts, 8. (Cantor Lectures). "The Thermo-chemistry of the Bessemer Process," by Prof. W. N. Hartley, F.R.S.

Tuesday, 23rd.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.

Wednesday, 23rd.—Society of Arts, 8. "The Preparation of Meat Extracts," by C. R. Valentine.

Thursday, 24th.—Royal Institution, 3. "Recent Researches in Magnetism and Diamagnetism," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.

Friday, 25th.—Royal Institution, 9. "Canterbury Cathedral" by The Very Rev. The Dean of Canterbury, F.R.S.

—— Physical, 5. "On the Circulation of the Residual Gaseous Matter in a Crookes Tube," by A. A. Campbell Swinton. "On some Improvements in the Roberts-Austen Recording Pyrometer, and Notes on Thermoelectric Pyrometers," by A. Stansfield.

Saturday, 26th.—Royal Institution, 3. "Portraits as Historical Documents," by Lionel Cust, M.A., F.S.A.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Gold Deposited on Iron.—Can anyone explain how gold is deposited on metallic iron? The facts of the case are as follows:—A piece of iron was taken from a pool of water (which contained copper in solution). After the copper was knocked off the iron the gold was exposed in very small plates. I have tested the gold with the usual tests.—B. H. B.

WILLESDEN DISTRICT COUNCIL.

SUPPLY OF SULPHATE OF ALUMINA.

The WILLESDEN DISTRICT COUNCIL are prepared to receive Tenders for the Supply of SULPHATE OF ALUMINA for the Treatment of Sewage in the Brent District for the year ending March 31st, 1899.

All particulars may be obtained on and after Monday, March 14th, 1898, upon application to Mr. O. Claude Robson, M.Inst.C.E., Engineer to the Council, Public Offices, Dyne Road, Kilburn, N.W.

Tenders, endorsed "Sulphate of Alumina," to be delivered not later than 4 p.m. on Tuesday, March 22nd, 1898.

The Council do not bind themselves to accept the lowest or any tender.

(By Order)

Public Offices, Dyne Road, Kilburn, March 8th, 1898.

O. CLAUDE ROBSON, Engineer to the Council.

COUNTY BOROUGH OF SALFORD.
GAS DEPARTMENT.

TENDERS FOR SULPHURIC ACID.

The GAS COMMITTEE invite Tenders for the Supply of about 1400 tons of SULPHURIC ACID, to be delivered during twelve months from date of acceptance of Tender. Full particulars may be obtained from the Gas Engineer, Gas Offices, Bloom Street, Salford. Sealed Tenders, endorsed "Tender for Acid," addressed to the Chairman of the Gas Committee, to be delivered to me not later than 3 p.m. on Thursday, March 24th, 1898.

(By Order)

Town Hall, Salford, March 12th, 1898.

SAML. BROWN, Town Clerk.

COUNTY BOROUGH of WEST HAM.

The COUNCIL of the Borough hereby invite APPLICATIONS from duly qualified persons for the following position on the Teaching Staff of the TECHNICAL INSTITUTE now in course of erection:—

HEAD OF THE CHEMICAL DEPARTMENT.

Full particulars of the duties attached to the post and of the salary to be paid may be obtained on application to the Principal of the Technical Institute, Town Hall, West Ham, E., before March 31st.

By order of the Council,

FRED. E. HILLEARY, Town Clerk.

Town Hall, West Ham, E., March 16th, 1898.

THE RESEARCH SOCIETY,

An International Association for the Advancement of Knowledge.

GOLD MEDALS, 1898.

AT the end of the current year, Gold Medals will be awarded for eminent philosophical work, experimental or logical, in connection with—

1. The Constitution of Matter.
2. The Medium of Physical Action in Space.
3. The Interaction of Cosmical Bodies.
4. The Development of Industry,
5. The Nature and Phenomena of Life.
6. The Nature and Phenomena of Soul.
7. The Powers of Good and Evil in the Universe.

The awards will not be made by any Council or secret conclave, where dogma, envy, hatred, malice, and all uncharitableness may have sway. Each Medal will be given in accordance with the free and open votes of all the Fellows of the Research Society, and will thus be a *real* honour.

The first number of "Research"—the Society's journal—is now in course of preparation. Papers are invited from all persons who have any discovery or argument to announce in any branch of Philosophy, whether physical, metaphysical, or extra-physical.

All communications should be addressed to the PRESIDENT OF THE RESEARCH SOCIETY, ARGENTAURUM LABORATORY, 30, CENTRAL AVENUE, NEW BRIGHTON, STATEN ISLAND, NEW YORK, U.S.A.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2000.

NOTE ON THE INTERACTION OF CYANIDES WITH THIOSULPHATES.

By LEONARD DOBBIN, Ph.D.

The fact that an interesting change takes place when potassium cyanide and sodium thiosulphate are intimately mixed with each other in concentrated solutions was accidentally discovered, a short time ago, in the analytical laboratories here. The discovery was due to the circumstance that numerous students, in examining a certain mixture, designed as an exercise in qualitative analysis and containing these two salts along with other ingredients, altogether failed to detect the salt-radical of the thiosulphates, and were able to find traces only of that of the cyanides, whereas the indications of the presence of sulphites and of thiocyanates were strongly marked and unmistakable. A very short investigation of the matter showed that a simple change takes place whereby the thiosulphate parts with one-half of its sulphur and is converted into sulphite, while the cyanide is simultaneously converted into thiocyanate. The following equation represents the change that takes place when potassium salts are employed:—

$$K_2S_2O_3+KCN=K_2SO_3+KCNS.$$

One part by weight of purified potassium cyanide (quite free from thiocyanate) was ground up in a mortar with 3·2 parts by weight of crystallised potassium thiosulphate, and the resulting pasty mass was preserved in a closed tube. Immediately after mixing, a part of the mixture was dissolved in water, hydrochloric acid was added in slight excess, and then a drop of ferric chloride solution, but no thiocyanate reaction was observable, neither could any sulphite be detected. After twenty minutes the ferric chloride test was repeated with a fresh portion of the mixture, when quite distinct evidence of thiocyanate was obtained. On the following day the thiocyanate reaction was strongly marked, as was also that of sulphite, but cyanide and thiosulphate were evidently both present also, although the thiosulphate reaction was rather faint. After a week the presence of thiosulphate in small quantity was still recognisable on boiling some of the mixture with dilute hydrochloric acid, but the reaction of cyanide could no longer be obtained. This final test showed that the cyanide had been completely transformed into thiocyanate, and that the thiosulphate had been employed in slight excess from the beginning.

What seemed to be the most likely places in the literature have been examined with a view to finding any reference to this interaction as having been previously described, but so far entirely without success. It is therefore believed to be novel, and it is for this reason that it is now placed upon record.

Chemistry Department, University of Edinburgh,
March 14th, 1898.

SOME STRIKING LECTURE EXPERIMENTS, WITH INDICATORS.

By JOHN WADDELL.

In the course of an investigation on Indicators, the details of which are given in the March number of the *Journal of Physical Chemistry*, I have come upon some striking experiments, which can be shown upon the large scale and are suitable for lecture purposes. They illustrate how the ordinary action of indicators used in alkalimetry may be completely masked by the addition of certain solvents.

The reactions are similar to that shown by cobalt chloride, which in alcoholic solution is blue, while the aqueous solution is pink. If water be added, in comparatively small quantity even, to the alcoholic solution, the pink colour appears, but the blue may be restored by the addition of ether. The phenomena are explained on the hypothesis that the dissociated salt of cobalt is pink and the undissociated salt blue, and that, in the presence of sufficient excess of alcohol or ether, the dissociation is diminished, giving the blue colour.

Cyanine in aqueous acid solution is colourless; but if a solution of cyanine be made in concentrated acetic acid, addition of alcohol or acetone turns it the blue colour which gives the substance its name. Water discharges the colour, which can be reproduced by further addition of alcohol or acetone, and the alternations of colour can be repeated almost indefinitely provided the reagents are not added in too great excess.

Methyl orange in acetic acid solution is red, but on addition of alcohol or acetone turns yellow (the same colour as in alkaline solution), but becomes red again on addition of water. The colours may be made to alternate as in the case of cyanine.

Paranitrophenol in ammoniacal solution is deep green; but if *concentrated* aqueous solution of ammonia is added to the paranitrophenol, acetone is capable of making the colour much lighter, and the further addition of ether discharges the colour entirely. Addition of alcohol, or more especially water, to the liquid thus obtained, produces an intense green.

It will be noticed that alcohol acts in this case like water, and not like acetone, the amount of dissociation in alcohol being sufficient to yield the colour of the ion.

Phenolphthalein in concentrated solution in acetone is scarcely coloured by addition of a considerable quantity of strong ammonia solution, but the further addition of water produces the very intense red characteristic of the alkaline solutions of this indicator.

If a solution of corallin in concentrated ammonia be made, addition of acetone will discharge the red colour, replacing it by a pale yellow, which turns back to red on addition of a little water, becoming once more yellow by addition of sufficient acetone.

The quantity of acetic acid or strong ammonia may be as large as 2 or 3 per cent of the total liquid.

It is to be specially noted that acetic acid and ammonia must not be replaced by hydrochloric acid and potash, as it is only with weak acids and bases that the phenomena can be readily observed.

Cornell University.

SEPARATIONS FROM CHROMIC ACID.

II. The Separation of Manganese.

By HARRY BREARLEY.

On adding potassium chromate to a neutral solution of a manganous salt there is no precipitate formed immediately, but on standing a dark brown precipitate is deposited. This precipitation is accelerated by heating, or if the operation be performed in a hot solution the precipitate forms at once. Various formulæ have been given to explain this reaction.

A circumstance in connection with manganese which does not obtain in treating iron or aluminium, is that the hydrate of a manganous salt exerts a strong reducing action, which is apparent from the well-known blackening of freshly precipitated $Mn(HO)_2$. Such hydrates formed

in a chromate solution would still more readily be oxidised, and cause the reduced chromic salt to be precipitated along with the manganese. Such, I imagine, is the cause of greater deficiencies than can be ascribed to the K_2CrO_4 and $MnCl_2$ reaction whenever the manganese salt is precipitated as hydrate.

Separation with Soda Hydrate.

In this and the following cases half a grm. of manganese (added as $MnCl_2$) is separated from 50 c.c. of a potassium chromate solution, after making acid and diluting to about half a litre. In no case was it possible to distinguish the precipitate as the white manganous hydrate, partly perhaps on account of the colour of the chromate, but more probably on account of its immediate oxidising effect.

It will be seen, from Table IV., that the usual increasing recovery attends the use of increasing amounts of alkali, and that the results are worse in hot than in cold solutions, though this latter may be due to the more energetic oxidising effect of the chromate in hot solutions, as well as to the increased vivacity of the reaction between the chromate and the manganous chloride. After filtering off a fraction of supernatant liquid the residue was poured into a strongly acidified solution of ferrous ammonium-sulphate, and titrated. Now, if the oxidation of the manganous hydrate had taken place solely at the expense of the chromate, the residue should have recorded an equivalent of K_2CrO_4, which—with that in the fraction of its supernatant liquid—would make up the total amount of chromate added. In every case this amount was exceeded, so that, in spite of being suspended in an oxidising liquid, which it did not completely reduce, the manganous hydrate absorbed oxygen from the air also. The chromate value of this atmospheric oxidation of the cold precipitations are given in the table.

TABLE IV.

Excess 2N.NaHO.	K_2CrO_4 found in filtrate. Boiling solutions.	K_2CrO_4 found in filtrate. Cold solutions.	K_2CrO_4 value of atmospheric oxidation.
1	3·4	16·4	14·3
10	7·7	21·1	15·7
20	10·0	29·0	17·2

In the hot solutions the atmospheric oxidation was much less.

This unpromising reaction has not, that I know of, been directly applied to the separation of manganous salts from chromic acid, but it seems to form a very serious drawback to an improved form of a well-known method of estimating chromium in steel, ferro-chromium, &c.

In 1877 (CHEMICAL NEWS, xxxv., 151) W. Galbraith described a method for estimating the chromium which was at that time being first introduced into steel. It consists briefly in dissolving the sample in dilute sulphuric acid, oxidising the Fe_2 to Fe_3 and the Cr_2O_3 to CrO_3 with permanganate, filtering off the manganese oxides, and titrating the chromic liquor with a ferrous salt and bichromate. With some slight modifications the method is still, at any rate in Sheffield, much used. In 1893 (*Journ. Iron and Steel Inst.*, i., 146) Galbraith deals with some objections which had been repeatedly urged against his method, but we are concerned only with the means he takes to free the precipitated manganese oxides from the chromic acid which it was said they retained. He might have reduced the needlessly large bulk of the oxides by adding less permanganate in excess, a procedure we had long before found to minimise the error; but he proposed instead to make the solution alkaline with soda hydrate before filtering, and then to wash the precipitate free from chromic acid. Mr. Galbraith's improved process, quoted *verbatim*, thus becomes:—"Dissolve in sulphuric acid (1 to 6), add permanganate, and boil till precipitate is black; then dilute and make alkaline with caustic soda, filter, wash,* acidulate filtrate, and treat as before with the ferrous salt and potassium bichromate.

The method is illustrated by reducing and re-oxidising a standard solution of bichromate: this particular test I have repeated with fair results, but it must be pointed out that it is not fully representative of the conditions under which the method is intended to be applied. For instance, take a chrome steel; the dissolved sample consists of ferrous and chromic sulphates, and unless the equation—

$$2FeSO_4+4H_2SO_4+2KMnO_4= \\ =Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+4H_2O$$

wofully misrepresents the facts, there exists, after treating with permanganate, no inconsiderable quantity of manganous sulphate, which, on the subsequent addition of caustic soda, would be precipitated as the energetic reducing agent $Mn(HO)_2$, which, as is shown above, disputes the claim of the separation to be called qualitative even.

It is noticeable that the mere separation of the iron cannot be dismissed with the indefinite "make alkaline with caustic soda": there needs be more than a faint excess of soda.

I have made trials on artificial and actual examples of chrome steel, and have obtained results in keeping with the above explanations.

Mr. Galbraith further illustrates the improved method by results obtained on samples of ferro-chromium *said* to contain certain percentages, but he nowhere adopts the more satisfactory course of dissolving a pure carbon steel along with a known quantity of a chromium salt. In one case he treats 5 grms. of a sample said to contain 8 per cent Cr, and finds by his improved process that it contains 9·5 per cent. If the sample did really contain 9¼ per cent, there was surely in the oxidation of the accompanying iron enough manganous sulphate formed to give the reducing action of the $Mn(HO)_2$ an opportunity of impressing itself on the observation. It may be recalled that larger excesses of alkali gave larger recoveries, and perhaps the same may be said for the permanganate; one can only suggest, in despair of offering a trusty explanation of Mr. Galbraith's results, that he uses these reagents in unusual excess: it may, at any rate, be set down that the process needs stating in more definite terms before it can be satisfactorily worked.

Separation with Bromine and Ammonia.

The advantage of this means of separating the manganese over the previous one consists in the presence of an oxidising agent ready to share the oxidation of the precipitated $Mn(HO_2)$ with the chromate. The separations are the better the more bromine there is present and the greater excess of ammonia there is added. Indeed an approximate accurate separation can be effected by using large quantities of these reagents, but the process is not to be compared with the following ones. Crookes ("Select Methods," p. 232) notices that when bromine is replaced by hydrogen peroxide or an hypochlorite, and the ammonia by soda, the manganese dioxide always contains chromium.

Separation with Soda Carbonate.

This reagent was added to boiling solutions of manganous chloride and potassium chromate; contrary to the behaviour of any other precipitant, an increased excess gave a decreased recovery. Soda carbonate was added also to a cold solution of the two salts and raised to boiling, and to a third set it was added; these last were filtered without any heating whatever. In the first case all the precipitates were dark coloured, but increasingly so as the alkali went up. In the second case the precipi-

* The precipitate would contain the excess of permanganate as manganese oxides, the oxidised $Mn(HO)_2$ precipitate, and the iron as ferric hydrate. When several grms. of a sample are taken these make up an enormous precipitate, which I am convinced cannot be *thoroughly* washed without great trouble.

tates were drab-coloured, and in the third case they might be described as creamy. The percentage recoveries are set forth in—

TABLE V.

Excess 2N carb.	Boiling.	Cold-boiling.	Cold.
1	85·0	96·6	96·5
10	68·4	99·3	100·3
20	63·8	99·8	100·2

Sell's process ("Select Methods," p. 128) for estimating chromium consists in oxidising the chromic oxide with permanganate, adding alcohol and a slight excess of soda carbonate, filtering off the manganese, and titrating the filtrate. This method is illustrated by Table V. only in so far as the manganous salts formed by the oxidation of the chromic oxide are concerned, and, except with very large amounts of chromium, the error due to precipitating from hot solutions might be overlooked.

Separation with Soda Phosphate.

Gibbs's (CHEMICAL NEWS, xvii., 195) instructions for precipitating manganese as the double phosphate of manganese and ammonia are:—"Disodic ortho-phosphate is to be added in large excess above the quantity required to precipitate the manganese as ortho-phosphate. This precipitate is re-dissolved in HCl or H_2SO_4, the solution heated to boiling-point, and ammonia added in excess. A white or semi-gelatinous precipitate is produced, which, on boiling or standing for some time, gradually becomes crystalline."

This process, applied to the separation of manganese from chromic acid, gives perfectly accurate results. If the soda phosphate be only in slight excess the results are a little low; if the ammonia, too, be only just in excess, the results are somewhat low; but an excess of 50 per cent phosphate and 20 c.c. normal ammonia, or more, always gives accurate results. This conclusion is based on a series of tests, in which each reagent was varied in turn: the above general statement may take the place of test separations which show no strong contrasts.

The crystallisation of the ammonia manganese phosphate facilitates the estimation of the manganese; but if only the amount of chromic acid is sought for, it is unnecessary to wait for the precipitate to form the beautiful talcose scales, pearly in lustre and pale rose in colour; it is unnecessary even to re-dissolve the first formed precipitate: simply add soda phosphate, make alkaline, and, after settling, syphon a portion through a filter.

LABORATORY NOTES.

By H. JERVIS.

Reducing Action of Filter-papers.

THERE is no need to state this fact with respect to many oxidising agents, but with respect to bichromate solutions there is some difference of opinion. Thus Arnold ("Steel Works Analysis," p. 154), when estimating Cr by a modification of Galbraith's method, filters the hot chromate solution through a *pure* paper, although in a footnote he draws attention to the fact that thick filters of impure paper are liable to reduce a little CrO_3 to Cr_2O_3, pure and ashless being apparently synonymous terms. I was recently made aware that one of the parties contending hotly over a difference of a few tenths per cent in a rich ferrochrome had filtered the hot chromate liquor through paper, unconscious of a possible reducing action.

To illustrate the point we have heated 25 c.c. of a solution of K_2CrO_4 (1 c.c. = 0·01 grm. Fe), diluted to 200 c.c. in a water-oven, then added a 12½ c.m. paper, and continued the digestion for half an hour. In one case the solution was made acid with 50 c.c. normal H_2SO_4, and in the other alkaline with 50 c.c. normal NaHO. A few cases in which the paper was added to a cold solution are also given:—

12½ c.m. Paper.	Ash.	c.c. K_2CrO_4 after digesting Hot.		Cold.	
		Acid.	Alkali.	Acid.	Alkali.
English (Ford Mill, 428)	0·0048	23·7	24·8		
Schleicher & Schüll (No. 589)	0·0003	23·8	24·2	25·0	25·0
Thin German (S. & S.)	0·0028	24·2	24·6		
Ordinary ,, ,,	0·0028	23·6	24·6	25·0	25·0
Swedish (Munktell) ..	0·0005	24·6	24·9		
French White	0·0070	24·3	24·7		
French Grey	0·0139	22·5	24·0	24·4	24·7
White Blotting (Ford Mill, 428)	0·0095	22·9			

Bottle Labels.

The ordinary unprotected adhesive label does not long resist the attack of damp acid fumes which are always in the air of an active laboratory. Of the varnishes, balsams, &c., used to coat the surface, paraffin wax is about the most handy and serviceable.

Faraday recommended a mixture of Brunswick black with half its bulk of oil of turpentine; the mixture to be kept in a bottle whose stopper was perforated with a thick nibbed pen. A more tasty label of a similar sort may be made by grinding sealing-wax, first dry and then mixed with a little alcohol and ether in such proportion as to make a thick liquid. Such liquid is best applied to the bottle with a small stiff brush. If the bottle can be warmed it is feasible to write on the heated surface with the pointed end of a piece of sealing-wax. Such labels never "gang agley," as the most carefully varnished paper labels sometimes do.

Tests for Sulphurous Acid.

In reducing ferric solutions with sulphurous acid the sense of smell does not indicate the absence of SO_2 with sufficient delicacy; it is prone to be biased by colds in the head and other physiological derangements. To boil for an inordinate length of time after this test has given negative results, so as to make sure, is rather rule-o'-thumb. Because it is easy to apply, I propose, instead of a Bunsen valve and other like contrivances, that through the hole of the stopper which closes the mouth of the flask there be inserted the short end of a syphon-like tube; as soon as the evolution of SO_2 becomes faint, the other end drawn out is dipped into an acid solution of very dilute permanganate. A decolorisation which gives place to a brown precipitate is not to be regarded, but the complete clearing of the solution indicates SO_2. This test, on account of large volume of vapour condensed, shows SO_2 after the sharpest noses have failed to detect it. The solution may be conveniently cooled and diluted by dipping the tip of the leg into cold water.

Interference of Manganous Salts with the Bichromate Estimation of Iron.

When a process fails, one naturally enquires after the author, but I am unable to find who is responsible for the suggestion that traces of iron may be estimated in the ignited Mn_3O_4 by dissolving in HCl, reducing, and titrating with bichromate. Such a procedure, however, I have seen practised—and, up to 1893, having unquestioned confidence in my superiors, I practised myself. I then had occasion to observe that the non-appearance of the blue colour was not a satisfactory proof of the absence of ferrous salts. The results of closer observation showed that a moderately strong solution of a manganous salt gives a brown colouration with ferricyanide, and that in presence of very small amounts of ferrous salts the blue colour may appear but momentarily and then give place to the brown colouration, or not appear at all. Thus, with as much Mn_3O_4 as one obtains from 1½ grms. of a 20 per cent spiegel, it was found after dissolving in HCl

and diluting to 100 c.c. (many times greater bulk than I have seen employed) that ferrous sulphate equivalent to 0·003 grm. Fe_2O_3 could escape detection. In very dilute solutions the Mn does not give a brown colour with ferricyanide, and hence the use of a very dilute solution of ferricyanide—used, say, ½ c.c. at a time instead of in drops—enables us to avoid the interference, but this device somewhat impairs the delicacy of the reaction. As some much-used processes include titrations of diluted ferrous salt in presence of manganese, it was thought worthy to notice this source of error, although the particular operation in connection with which it was observed may have grown obsolete. When using the sulphocyanide colour test, the presence of manganese introduces a slight negative error of no practical importance. It may be interesting to notice that the presence of manganese chloride heightens the accuracy of a proportional contrast; that is, solutions of equal volume, containing respectively 0·0001 and 0·0003 grm. Fe, are more nearly alike in tint than when the latter is diluted three times in presence of $MnCl_2$ than without it.

ON THE OCCURRENCE AND EXTRACTION OF THORITE, MONAZITE, AND ZIRCON.*

By P. TRUCHOT.

THE recent progress made in gas-lighting depends on the principle of producing a complete combustion of the hydrocarburetted materials and using the great amount of heat thus produced for rendering incandescent certain oxides selected and arranged in the most suitable manner.

Many *savants* have been working on this idea for some years, but without good results. It was not until a few years ago that Auer von Welsbach, inspired by the work of earlier chemists, succeeded in producing in an elegant and practical manner a method of applying the then rare oxides to the purpose of incandescent gas lighting.

The present Auer mantles are composed of about 99 per cent of oxide of thorium and 1 per cent of oxide of cerium; while the former ones, dating from 1883, were formed, above all, of oxide of zirconium and oxide of lanthanum.

These rare oxides, the basis of the incandescence, are very difficult to obtain, and we propose in this article to study the principal minerals now being used for their production, namely, thorite, monazite, and zircon. We shall give their composition as well as their principal sources.

I.—*Thorite.*

Thorite is a hydrated silicate of thorium; its formula is SiO_4Th+2H_2O. It contains a small amount of oxides of iron, manganese, calcium, magnesium, lead, tin, and a fairly noticeable amount of oxide of uranium.

In nature it is found in the form of dodecahedric crystals with two tetrahedric faces, unequally developed, or of an hexagonal appearance.

It is in colour darkish brown or orange (one variety being named *orangite*); it has a resinous lustre and a conchoidal fracture. In thin flakes it is translucent or transparent.

It has been found in syenite at Lowö, near Brewik, in Norway; but the only deposits really known and worked for the manufacture of mantles are those of Langesundfjord, between Arendal and Christiania.

Table I. shows the average composition of two samples of thorite and one of orangite from these Norwegian deposits.

TABLE I.—*Average Composition of the Minerals of the Thorite Group.*

	Orangite.	Thorite.	Thorite.
Silica (SiO_2)	17·32	18·98	17·04
Oxide of thorium (ThO_2)	71·65	57·91	50·06
Oxide of uranium (U_2O_3)	1·13	1·58	9·78
Oxide of lead (PbO)	0·88	0·80	1·67
Sesquioxide of iron (Fe_2O_3)	0·59	5·79	7·60
Alumina (Al_2O_3)	0·17	0·06	—
Oxide of cerium (Ce_2O_3)	—	—	1·39
Lime (CaO)	1·59	2·58	1·99
Magnesia (MgO)	traces	0·36	0·28
Alkalis	0·47	0·24	—
Water (H_2O)	0·14	9·50	9·46
Density	5·19	4·80	4·38

II.—*Monazite and Monazite Sands.*

Monazite is essentially an anhydrous phosphate of cerium, lanthanum, and didymium; its formula may be represented by $(CeLaDi)_2O_3P_2O_5$ (Penfield). It always contains—and this is what makes it valuable from our present point of view—variable quantities of oxide of thorium, which may exist in the form of silicate, as in thorite and orangite, or as a phosphate forming a double salt with phosphate of cerium, or even as an amorphous mixture.

Monazite contains a small quantity of zirconia, alumina, magnesia, lime, oxides of iron, manganese, tin, and lead, besides small quantities of titanic acid and fluorine. It crystallises in clinorhombic prisms, either translucent or transparent, of a yellowish, reddish yellow, brownish, or greenish colour, with a resinous lustre. The brownish or yellowish fragments appear to be the richest in oxide of thorium.

This mineral which, as recently as three years ago, was considered to be extremely rare, has become relatively common—thanks to the discovery of such enormous deposits of monazite sands—that even the incandescent gas-lighting industry may very reasonably have disappeared before one thousandth part of it has been used.

Monazite has been found in large quantities in the United States, Canada, and Brazil; it has also been noticed in England (in Cornwall). It has been met with in Sweden, at Holma, Karafoet, and Johannisberg; in Norway, at Arendal, Hitteröe, Noterö, and Midbö; in Russia, in the Ilmen Mountains and in the placers of the river Sanarka; in France it has been found at Puy, near Saint Christope; and, finally, a mine has just been discovered at Ryfilke, in Norway.

In each of these deposits the monazite is one of the secondary constituents of the eruptive rocks, granite and gneiss. It has been found in a large number of similar rocks, and a more careful study will certainly reveal the fact, in a few years, that all granites and gneiss contain it in more or less quantities. All the most important deposits (the United States, Brazil, Siberia, &c.) thus come from the disaggregation of the primitive granitoid rocks under the influence of variations of temperature, erosion, &c., and are, as a rule, found localised in beds, or at the source of small rivers, and on the sea-shore.

The monazite originating from the destruction of these rocks is naturally mixed with a number of other minerals, which form with it what is known commercially as the *monazite sands*.

The principal minerals present are—*Zircon* (which is always present, and often in larger quantities than the monazite), then *xenotime*, *fergusonite*, *sphene*, *rutile*, *garnet*, *brookite*, *ilmenite*, *apatite*, *magnetite*, and sometimes *corundum*, *colombite*, *samarskite*, *gadolinite*, and *orthite*.

The most important deposits of monazite sands actually known can be divided into two principal groups:—(1) Those in the United States and Canada; (2) those of Brazil, Columbia, and the Argentine Republic.

* *Revue Générale des Sciences*, No. 4, February 28, 1898.

Deposits in the United States and Canada.

The deposits in the United States are mostly in North Carolina, but some are in South Carolina and Virginia, while it has quite recently been discovered in the State of Idaho.

1. *North and South Carolina.*—The area covered by these deposits is about 1600 square miles, spreading over the counties of Burke, McDowell. Rutherford, Cleveland, and Polk (North Carolina), in a part of the county of Spartanburg (South Carolina), and in the county of Amelia (Virginia). The principal deposits of this region are in the Silver, North Muddy, and South Muddy streams, the Catawba river, the Second Broad River, and the First Broad River (Rutherford, Cleveland, and Spartanburg). All these rivers have their sources in the mountains in the south, not far from the Blue Mountains. The rock is composed of granite, biotite, gneiss, diorite, and hornblende, cut almost at right-angles by a parallel system of small veins of auriferous quartz. The greater part of this region has been worked for gold.

It was in 1879 that, for the first time, Mr. W. Hidden found workable quantities of monazite. These are, as a rule, found at the sources of the above-named rivers mixed with gravel and ordinary sand. The thickness of the deposits of these monazite sands is from 0·3 to 0·6 metre, while the breadth of the streams is often 3·6 metres. The proportion of raw monazite present is extremely variable, oscillating between merely traces and 1 or 2 per cent. Naturally the richest deposits are nearer the source of the streams—the heavier minerals, particularly monazite, being concentrated there.

The monazite from these deposits, as we learn from a memoir by Mr. Nitze, is extracted by washing the sand and the gravel in sluices—exactly in the same manner as for alluvial gold. The sluice boxes are about 2·4 metres long by about 0·5 metre in width, and about 0·5 metre in depth. Two men work the sluice box; one shovels the sand on to a perforated screen fixed at the upper extremity of the apparatus, while the other keeps the material inside in constant movement, either with a fork or a perforated spade, in such a manner as to eliminate the less dense sands. These boxes are cleaned up at the end of every day's work; the washed and concentrated monazite being collected and dried.

If the sand obtained contains magnetic iron, the latter can be removed by means of a strong magnet, but the greater part of the heavier minerals cannot be eliminated —there is always zirconium, rutile, brookite, corundum, garnet, &c., remaining. Commercial monazite sand thus prepared is not pure, but is only a mixture of heavy minerals in which monazite predominates. A sand containing from 65 to 70 per cent of monazite is considered to be of very good quality. A good daily return varies from 18 to 32 kilos. of monazite sand per sluice box.

As there are but few regular mining undertakings existing in this region, as a rule each claim holder works his own claim, and sells the monazite to the local buyers —or, as often happens, exchanges it for produce.

As a matter of fact, with but few exceptions, the monazite deposits in the river beds have been almost entirely exploited; it follows, then, that the operations are now directed to the deposits of gravel in the adjacent valleys.

These deposits are worked by small shafts about 0·75 of a metre square, which enables the sand to be extracted and put in the sluice box arranged at the mouth. The upper layers are generally rejected, except when they are found to contain a little monazite. The shafts are arranged in parallel lines, similar to the method adopted in gold placer workings. At the Blanton mine, on the Hickory river, two miles north-east of Shelby, in Cleveland county, the deposit is from 90 to 120 metres in width, and has been partly worked for a distance of a quarter of a mile along the bank of the river. The upper layer has a thickness of 0·9 to 1·0 metre, and the layer of monazite sand 0·3 to 0·9 metre.

In the county of Spartanburg, in South Carolina, the extraction and concentration by washing and deposition are carried out in a much more perfect manner, and, although the raw sands contain a much larger proportion of garnet, rutile, and titanic iron, the commercial product is obtained much more economically in the form of monazite sands of different grades.

Two sluice-boxes, one placed above the other, are used for the washings. The sand is shovelled on to a perforated plate fixed at the upper end of the first box, and a subsequent washing gives a sand of great purity, often containing 85 per cent of monazite. The tailings from this washing (the lighter particles) are discharged directly into the lower box, where they are washed over again and give a sand of the second grade.

These sands are almost always further treated by machines similar to those used for winnowing wheat. In this manner a black sand is separated consisting of quartz and very fine fragments of monazite, which constitutes the final tailings. It is impossible to further wash these sands without a loss of monazite, or to separate any more of the garnet, rutile, or titanic iron which must always be present, even in the best samples.

If the monazite gravel contains gold this latter will be found with the monazite, and this is by no means rare, since in most auriferous placers monazite has long been found in the residue thrown on one side from the washings of the gold-bearing sands.

(To be continued).

THE SIMULTANEOUS VOLUMETRIC ESTIMATION OF SULPHURIC ACID AND LIME IN WATERS.

By LUCIEN ROBIN.

I HAVE attempted the rapid estimation of the sulphuric acid and the lime in waters; these two bodies being of much importance, as much from the point of view of potability as for use in boilers.

We take 100 c.c. of the water to be analysed and place it in a specially shaped flask having an expansion in the neck above the 100 c.c. mark, add ½ c.c. or 1 c.c. of the alkaline solution used in the estimation of the ammonia by Nessler's solution,* then boil gently for about five minutes; cool under the tap, bring up to 100 c.c. again, shake thoroughly, and filter exactly 50 c.c. The filter and the funnel are placed over the special flask.

Estimation of the Sulphuric Acid.—We use the well-known method of precipitation by a known quantity of chloride of barium, then titrating by chromate to measure the excess. We prefer to work in the following manner:— To the 50 c.c. of the filtered solution we add two drops of litmus and acidulate with five or ten drops of pure hydrochloric acid, and boil for three or four minutes to drive off the carbonic acid. We then add a few drops of ammonia to neutralise the acid, and, without taking away the flame, pour in exactly 10 c.c. of a N/20 solution of $BaCl_2,2H_2O$, then withdraw the heat and allow to stand for fifteen minutes. After this time, boil and add 10 c.c. of a N/20 solution of chromate.† After a few minutes' boiling, cool under the tap and filter. The flask must be washed out twice with enough water to fill the filter each time.

* Pure crystallised carbonate of soda, 100 grms.; caustic soda in alcohol, 50 grms.; distilled water, 300.

† We weigh exactly 3·690 grms. of bichromate of potassium and dissolve it in water, saturate the solution with pure ammonia, and make up to 1 litre. It is necessary to make quite certain that 10 c.c. of this solution corresponds exactly to 10 c.c. of the solution of barium—but this is not a difficult matter.

To the filtrate we add 20 c.c. of a solution of ferrous sulphate (10 grms. of the salt and 20 c.c. of sulphuric acid per litre), then titrate the excess of the ferrous salt with decinormal permanganate of potash—let us suppose that we have used 3·3 c.c. of this latter. On the one hand, we take 5 c.c. of the chromate solution, to which we add 20 c.c. of the ferrous solution, and by means of permanganate we estimate the quantity of the ferrous salt unoxidised by the chromate, say, 16 c.c.

On the other hand, we estimate the quantity of permanganate necessary to oxidise 20 c.c. of the ferrous solution, say, 19·5 c.c. Thus, 19·5 c.c. − 16 c.c. = 3·5 c.c., corresponding to the iron oxidised. This understood, let us suppose that in an estimation we have used 3·3 c.c. of permanganate, we should then say 19·5 c.c. − 3·3 c.c. = 16·2 c.c., which would represent the quantity of permanganate corresponding to the ferrous salt oxidised by the chromate in excess, from which we deduce—

$$x = \frac{5 \times 16{\cdot}2}{35},$$

x being the number of c.c. of chromate in excess, from whence $x \times 0{\cdot}068 = CaOSO_3$ per litre of water; in fact, the number of c.c. of chromate in excess represents that of the solution of barium which was used to precipitate the sulphuric acid.

Comparative Estimations in M.grms. per Litre.

By weight.	Volumetrically.	Oxygen absorbed.*
11·0	9·0	1·0
70·0	72·2	4·1
349·0	343·0	4·0
396·4	398·0	5·8
641·3	639·2	6·3

* We give the oxygen absorbed by the organic matter to show that this latter has very little influence on the results.

Estimation of the Lime.—The filter which was used for the filtration in the estimation of the sulphuric acid is moistened with 5 c.c. of half-strength hydrochloric acid, and washed by filling up the filter twice with warm water. This is then made slightly ammoniacal, and we then add 10 c.c. of a solution of decinormal oxalate of ammonia. Make up to 100 c.c. and, after shaking, let stand for at least half an hour. After this time we can do one of the two following things:—(1) Estimate in an aliquot part—50 c.c., for example—the excess of oxalic acid after having filtered it and made it slightly acid with a little pure nitric acid; or (2) estimate the oxalic acid in the precipitate after having filtered and then washed twice with ammoniacal water, and finally with warm water. The filter placed over the flask where the precipitation was made is washed three times with 5 c.c. of pure dilute warm nitric acid. After the solution of the oxalate, we wash twice with boiling water, filling the filter each time, and in the liquid we estimate the oxalic acid after having heated it to about 60°. The number of c.c. of permanganate used × 0·028 give the total quantity of lime present in 1 litre of water.

Comparative Estimations in M.grms. per Litre.

By weight.	Volumetrically.
9·6	8·5
80·0	77·0
226·0	222·0
247·0	241·0

If the water contains much, it suffices to augment the quantity of the reagents used. If the *special* flask is not used, it is as well to boil in a flask gauged to 200 c.c. and make up to this amount, then filter 100 c.c. instead of 50 c.c. for estimating the sulphuric acid.

By this method, one can estimate several samples of water, both for sulphuric acid and lime, in less than an hour.—*Journal de Pharmacie et de Chimie*, Series 6, vol. vii., No. 6.

THE ACTION OF SULPHURIC ACID ON MERCURY.

By J. R. PITMAN.

The following statement is made by Messrs. Baskerville and Miller, in a previous number of the *Journal of the American Chemical Society* (xix., 874):—"A qualitative experiment showed that mercury decomposed concentrated sulphuric acid at the ordinary atmospheric temperature, about 20° C."

As a large amount of my work consists in the use of nitrometers, this statement was of considerable interest to me; however, believing their conclusions to be erroneous, the following simple tests were tried:—Apparatus used, a Lunge nitrometer, with separate reading burette; the temperature at all times was about 22° C.; the amount of mercury was from eight to ten times that of the acid (by volume).

First experiment: 30 c.c. of concentrated sulphuric acid was run into the generating bulb, and allowed to stand for forty-eight hours, being shaken at intervals. I was unable to get any gas at all under these circumstances, and there was apparently no reaction between the mercury and the sulphuric acid. Thinking that possibly the presence of air might have some effect upon the reaction, I next measured a certain quantity (about 50 c.c.) of rather damp mercury: this was run into the generating bulb and 30 c.c. of sulphuric acid as well; after shaking at intervals for twenty-four hours, the air was re-measured and found to have *lost* four-tenths c.c.: this loss was probably due to the presence of considerable moisture in the air when first measured; as a check this same air was conducted (thoroughly dried from its contact with the sulphuric acid) from the reading burette into another generating bulb, drawing in 30 c.c. of concentrated sulphuric acid, and shaking again, as before, for about twenty-four hours, with a result of a loss of less than 0·05 c.c., which is an error that might occur in any test.

In order to try the effect of the preponderance of sulphuric acid, 1 part of mercury to 70 by volume of concentrated sulphuric acid was taken (sp. gr. 1·84), introduced into a flask, and shaken violently for some time; no mercuric sulphate was formed, nor was there appearance of any other reaction; this was at a temperature of 25·5° C. From these experiments it is apparent that there is no reaction between mercury and sulphuric acid at ordinary temperature, and if Messrs. Baskerville and Miller found a reaction as they state, it must have been by means of some different method.—*Journal of the American Chemical Society*, vol. xx., No. 2.

THE DETECTION OF SALICYLIC ACID IN FOODS.

(Preliminary Note).

By F. A. GENTH, Jun.

In the examination of foods for salicylic acids to so-called distillation method, suggested by G. Krause and fully described by Mr. McElroy, is the one most frequently used.

The method is as follows:—The mass is pulped with phosphoric acid in a mortar, water added if necessary, and after some time strained through a cloth. About 50 to 75 c.c. of the liquid is then subjected to distillation and successive portions of 5 c.c. each of the distillate collected and tested with ferric chloride. If salicylic acid has been used as a preservative, it will be distilled with the water vapour, and give a violet colouration when ferric chloride is added. In the first portions of the distillate no reactions may be obtained, and in cases where only very small amounts of salicylic acid are present in the article under under examination, the reaction in the last portion of the

distillate would not be very marked. The methyl ester reaction, which is likewise recommended as a test for salicylic acid, cannot always be obtained when the amount present is small.

No other substances have been known to yield distillates giving similar colourations, or any reactions interfering with that for salicylic acid under the above circumstances.

The writer has recently had occasion to examine a series of preserves, such as jellies, jams, catsup, &c., for preservatives, Among the samples submitted were a number obtained through the courtesy of Food Inspector H. J. Hackett, and were known to be free from salicylic acid or other preservatives. In the examination of these latter samples according to the above-described method, a colour reaction similar to that given by salicylic acid was found in all cases. When tested with ferric chloride the first portions of the distillate showed little if any colouration, and only as the distillation continued did it become more marked. In many cases the distillation process was not continued to within the last 10 c.c., but was stopped with over 25 c.c. still remaining in the flask. The colouration in dilute solutions was violet, of about the shade and colour of similar ferric salicylate solutions; in more concentrated solutions the colour was much redder in the case of the distillate from the pure food, and was found to effectually hide the presence of small amounts of salicylic acid, when added.

The nature of the distillates and the examination of food-stuffs for salicylic acid will be further investigated.—*Journal of the Franklin Institute*, cxlv., No. 3.

DIASTATIC FUNGI AND THEIR UTILISATION

By JOKICHI TAKAMINE.

Up to the present time the germination of cereals has been the only source of diastase of any practical importance known in America and Europe. It is true that there is diastase of animal origin, such as ptyalin and pancreatic diastase, but their sources are limited and their potency unstable. Therefore they are comparatively of less importance than the vegetable diastase, which has an inexhaustible supply of raw materials of uniform power. In Japan, and some other Asiatic countries, certain kinds of fungi are used in the production of diastase. The fungus that is in use in Japan is called *Moyashi*, which was named by Ahlburg *Eurotium Oryzæ*. It belongs to the genus *Aspergillus*, and is distinguished from ordinary fungus by its remarkable power of generating diastase during its growth. It is a perfectly harmless plant, as proven by the fact that it has been used in Japan for several centuries in the manufacture of the various daily beverages. Further study has shown that a good many other fungi have, to a more or less degree, a similar property, and naturally, therefore, the selection of the species which has the strongest diastase generating power becomes of technical importance. This selection is determined by the culture, multiplication of each species, preparation of diastatic substance, and the comparison of the diastatic power of different species under similar conditions. Such selected species are then subjected to cultivation for the purpose of obtaining their matured spores in the production of diastatic substances. For this purpose suitable materials, such as rice, hominy, ground corn, or wheat bran, are thoroughly steamed so as to sterilise the mass, as well as to gelatinise the starch, and the product is supplied with an artificial fertiliser to give the plant the sufficient amount of nutriment for its complete maturity. On to this mass selected culture is sown, after which it is put into an incubator of proper temperature and humidity. Inside of twenty-four hours the fungus growth will become visible, and at the end of six or seven days the growth will reach its maturity, presenting a rich, velvety appearance of colour, varying from reddish to dark green, according to the species of plant used. This product is carefully dried and preserved. The matured spores of the plant may be separated from the mass by shaking or sifting, and then can be preserved indefinitely. The product thus obtained is called Taka-Moyashi, and is used as the seed spore in the manufacture of diastatic substances.

To produce diastatic substances for commercial purposes, wheat bran is first moistened with water and then thoroughly steamed. After the mass is cooled down below 40° C., a small quantity of Taka-Moyashi is added and thoroughly mixed. The mass is then taken into a growing-room similar to that of a malt-floor, and spread in a layer varying from 1 to 2 inches in thickness. The temperature of the room is kept at about 25° C., and the humidity at above 80 per cent. Inside of twenty-four hours the fungus shows its growth, and the diastatic strength of the mass will steadily increase as the growth advances, and it will be found that within from forty to fifty hours the diastatic power reaches its maximum, after which the mass is taken out of the growing-room and cooled down to ordinary temperature to check the further growth of the plant. The mass thus obtained is called Taka-Koji, and can be used as it is in the green state, or it can be dried for preservation. As the diastase generated in Taka-Koji is readily soluble in water, the mass may be percolated with cold water and the extract thus obtained can be used as a diastatic agent, or, for the same purpose, it may be mixed with the extract of ungerminated cereals, which have the singular property of augmenting the diastatic power of Taka Koji.

This extract, for the purpose of preservation, may be evaporated under a vacuum to a thick syrupy condition. In this condition its diastatic power is from eight to ten times stronger than that of malt extract of similar consistency. It can be applied to all such industries as the manufacture of alcohol, beer, vinegar, &c., where the diastase performs the important function of converting starch into sugars.

The aqueous extract of Taka-Koji can still be further purified by precipitating the diastatic principle of the extract by the addition of alcohol. For this purpose an extract containing about 20 per cent of solid matter is mixed with four to five times its own volume of strong alcohol. By this means the diastase, together with some other albumenoids, is precipitated, while the sugars and other impurities remain in solution. The precipitate is now separated from the mother-liquor by decantation and centrifugal force; it is then pressed and air-dried. The product thus obtained is called Taka-Diastase. It is a yellowish-white odourless powder, possessing a nutty taste. It is readily soluble in water, yet it is non-hygroscopic. It is perfectly stable in its diastatic power. It converts in ten minutes over 100 times its own weight of starch, according to the modified Junk's test. It has remarkable starch liquefying property besides starch-saccharifying property, the former being three or four times stronger than that of purified malt. It is strong enough for all practical purposes. It can be, however, further purified to wonderful strength by re-precipitation or otherwise.

The applications of Taka-Diastase are varied and extensive. From the remarkable stability of its diastatic power it can be used as a standard of comparison in the determination of the diastatic power of other substances. Its use as a remedy for amylaceous dyspepsia is of no mean importance.

Considering the fact that more than two-thirds of our food consists of starch substances, such as potato, bread, pudding, &c., and also that the diastase of the saliva has to perform the principal function in the digestion of starchy food, and that the saliva is subjected to loss and deterioration of its diastatic power from various causes, such as smoking, drinking, chewing, and rapid eating, it is not to be wondered at that two-thirds of the dyspepsia

is of a starchy origin, and therefore it is apparent that some kind of strong diastatic substance is required to supply the deficiency of the diastatic power in the system of the digestive organs.

While our knowledge is very limited of the quantitative estimation of the diastase daily generated, and contained in the saliva and pancreatic juices, as far as my investigation goes the quantity of diastase secreted in the saliva daily is very considerable. It amounts to from 5 to 8 grms. of Taka-Diastase, or about ½ pound of the best malt extract. While investigation in the way of the production of diastase from a fungus growth is still in its infancy, yet that which we already know on this subject seems to indicate that this has opened an entirely new field for the economic production of diastatic ferments. I firmly believe that this field will, in the future, supersede in every respect the old known source, namely, the germination of cereals.—*American Journal of Pharmacy*, vol. lxx., No. 3.

ALKYL BISMUTH IODIDES AND BISMUTH IODIDES OF VEGETABLE BASES.*

By ALBERT B. PRESCOTT.

THE common alkyl ammonium iodides, with solutions of the bismuth salts, give bright-coloured precipitates. As formed by quaternary methyl or ethyl ammonium iodides, the colour is orange-yellow in most cases, usually lighter when obtained with bismuth chloride, and darker when obtained with bismuth nitrate. When fully formed by excess of the organic iodide, in bismuth solution not strongly acid, the precipitation is amorphous and so nearly complete that when the filtrate from a test-tube portion is evaporated to dryness and the residue ignited and treated with solvent acid, hydrogen sulphide fails to blacken the liquid. Strong mineral acids slowly decompose these coloured precipitates, liberating iodine.

What has been known as Dragendorff's reagent for alkaloids is a potassium-bismuth iodide, prepared by dissolving precipitated bismuth iodide in a concentrated solution of potassium iodide acidulated with hydrochloric acid, and known as giving reddish coloured precipitates in solution of the salts of the alkaloids. On trial with pyridine salts, a corresponding precipitate was obtained, dark orange-red and voluminous. Kraut (*Ann. Chem.* (Liebig), ccx., 310—327) has reported the piperidine compound, to which all these are analogous.

These organic bismuth iodides are not perfectly proof against decomposition by much water; they are sparingly soluble in ethyl or amyl alcohol, insoluble in glacial acetic acid, in ethyl ether, in chloroform, and in benzene.

The tetramethyl ammonium-bismuth iodide crystallises from hydrochloric acid, that of sp. gr. 1·19 diluted with an equal measure of water. Also from potassium iodide solution acidulated with hydrochloric acid. The pyridine and the alkaloid bismuth iodides crystallise from alcohol. In all these cases the crystals are clearly hexagonal and easily obtained.

Both the amorphous and crystalline forms are stable in the air. A sample of tetramethyl ammonium bismuth iodide remained constant in weight at 130°; atropine bismuth iodide melts, but at 98° C. holds constant weight.

Reducing agents, as potassium thiosulphate, do not alter these bismuth iodides. Tetramethyl ammonium bismuth iodides, precipitated from 10 per cent solutions both of the organic iodide and bismuth iodide, washed with hydrochloric acidulated water, then with pure water till washings gave no residue, then with alcohol, and lastly with ether, and dried at 110°, gave figures as follows:—

Analyses I. and II. were of the same preparation; III. and IV., from other preparations made at different times.

	I.	II.	III.	IV.	$N_3(CH_3)_{11}HBi_2I_7$.
Iodine ..	58·71	58·29	60·79	—	59·22
Bismuth.	27·08	—	—	—	27·07
Carbon..	8·69	8·68	8·58	8·06	8·82
Hydrogen	2·16	2·12	2·30	2·37	2·08
Nitrogen.	2·81	2·73	—	—	2·81

The pyridine bismuth iodide, prepared from a pyridine salt by Dragendorff's reagent and crystallised from alcohol, on elementary analysis gave figures as follows:—

Different preparations.	I.	II.	III.	$(C_5H_5N)_3(HI)_3Bi_2I_6$.
Iodine	63·98	62·84	62·24	63·59
Bismuth. ..	23·36	23·72	—	23·18

Kraut (*Ann. Chem.* (Liebig), ccx., 310—327) found analogous composition for piperidine bismuth iodide.

The corresponding atropine bismuth iodide gave results as follows:—

Several preparations.	I.	II.	III.	$(C_{17}H_{23}NO_3)_3.(HI)_3Bi_2I_6$.
Iodine.. ..	46·99	47·03	46·51	46·96
Bismuth ..	18·82	18·67	18·53	17·22
Carbon ..	23·22	23·62	23·69	25·23
Hydrogen ..	2·87	3·02	2·94	2·96
Oxygen. ..	8·10	7·66	8·33	7·63

The carbon is too low for the theory, so that the figures approach to those of $(C_{17}H_{23}NO_3)(HI)BiI_3$.

The brucine compound gave, for—

$$(C_{23}H_{26}N_2O_4)_3(HI)_3Bi_2I_6,$$

of iodine 41·10 and 40·88 per cent, against 41·56 by calculation from the formula.

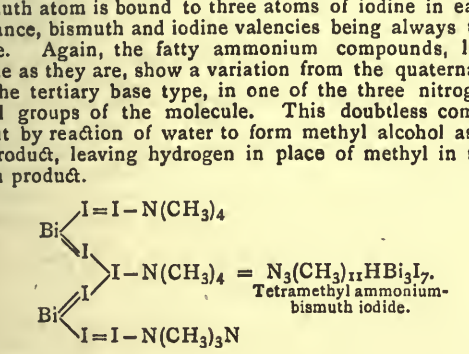
The corresponding strychnine salt gave, for iodine, 44·02 and 44·65 per cent against 44·48 by calculation from the formula.

In the results of the work I have done upon the perhalides and double halides of nitrogen bases in the last two or three years, everything goes to support the theory that two or more halogen atoms link to each other with an (uneven) valence of more than one, so as to connect one group of atoms with another. Iodine, especially among the halogens, serves as a binding element in the coupling of other elements with each other, as well as in massing its own atoms together in a heavy periodide, as a swarm of bees hang upon the bough of a tree. In the double iodide structure, where iodine links one base to another base, serving between positive and positive, with iodine not in excess of the "normal" number of its atoms, potassium thiosulphate will not take iodine out of the compound. In the periodide structure where iodine links a base to additive iodine, serving between a positive and a negative group, potassium thiosulphate promptly removes all the additive iodine, leaving a normal single iodide. These generalisations apply to the dipyridine alkyl iodides reported with determinations of molecular weight by Mr. Flintermann and myself in 1895 (*Journ. Am. Chem. Soc.*, xviii., 28). Also to the various monopyridine alkyl normal iodides (Prescott and Baer, 1896, *Ibid.*, xviii., 247) and to the numerous periodides (Prescott and Trowbridge, 1895, *Ibid.*, xvii., 859; P. F. Trowbridge, 1897, *Ibid.*, xix., 322; Trowbridge and Diehl, 1897, *Ibid.*, xix., 558). In the compounds of additive iodine, as in double iodides, the results of analyses are in most cases consistent with an uneven valence of iodine, indeed with its trivalence. But there are a very few periodides well determined by Mr. Trowbridge as monopyridine compounds, in which, in our present knowledge, an even numerical valence of iodine is indicated.

The bismuth iodides of nitrogen bases reported in this paper—both those of fatty alkyls, on the one hand; and

* Read before the American Pharmaceutical Association, in the report of a special committee, at Minnetonka Lake, August, 1897, and to be published in the Association *Proceedings* for this year. From the *Journal of the American Chemical Society*, xx., No. 2.

those, on the other hand, of pyridine and pyridine-derived alkaloids—all evidently conform in their analytical content to the regular iodine-linking structure—the structure common both to double iodides and periodides, as shown in the following proposed constitutional formula. In the case of the quaternary ammonium bismuth compounds, with the prevailing bismuth characteristic of losing halogen in presence of water, the wash-water being found tinged with iodine, each bismuth atom is directly bound to only two atoms of iodine, while in the pyridine-formed compounds the bismuth atom is bound to three atoms of iodine in each instance, bismuth and iodine valencies being always the same. Again, the fatty ammonium compounds, less stable as they are, show a variation from the quaternary to the tertiary base type, in one of the three nitrogen basal groups of the molecule. This doubtless comes about by reaction of water to form methyl alcohol as a by-product, leaving hydrogen in place of methyl in the main product.



The alkaloidal bismuth iodides are not quantitatively uniform enough to be entirely satisfactory for alkaloidal assay, but are more stable and uniform than the alkaloid mercuric iodides formed by Mayer's reagent. On the other hand, they are more bulky, less easy to gather in a compact mass, less manageable in filtration. On the whole, so far as found, Dragendorff's reagent gives no general advantage over that of Mayer, though I am well aware how unsatisfactory the latter has been found in the hands of analysts.

For the execution of the work upon tetramethyl ammonium bismuth iodide, I am wholly indebted to Mr. H. E. Brown; for that upon the bismuth iodides of pyridine and the alkaloids, to Mr. O. C. Diehl. A further study of the reactions of the halides of bismuth upon representative organic bases is now left to Mr. Brown.

NOTICES OF BOOKS.

Spectrum Analysis, by John Landauer. Authorised English Edition. By J. Bishop Tingle. First Edition, first thousand. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1898. Pp. 239. 8vo., 134 figures.

Dr. Landauer's excellent treatise first appeared as an article contributed to Fehling-Hell's "Neues Handwörterbuch der Chemie," and was published as a separate book at the request of a number of competent authorities. Dr. Tingle's translation now makes it available for English readers. Among the features of this very practical book are full bibliographical references to authorities suitable to the historical treatment of the subject. The older measurements, to secure uniformity, have been recalculated to accord with Rowland's system of wave-lengths.

A summary of the chapters will give a good idea of the contents of the book:—I. Historical Introduction. II. Physical Properties of Light. III. Spectroscopes. IV. Spectroscopic Instruments for Special Purposes. V. Spectroscopic Adjuncts. VI. Emission Spectra. VII. Spectra of the Elements. VIII. Absorption Spectra. IX. The Solar Spectrum. X. Other Celestial Bodies.

In Chapter VII. the wave-lengths of the spectrum lines of the several chemical elements are given very fully, in alphabetical order of the elements.

The book is notable for the very concise and clear style of the author, which has been admirably preserved in the translation; some paragraphs, as those in the last chapter, are very brief, yet they indicate the essential facts necessary for a student to know, without a superfluous word. For students having a knowledge of the elements of physics the book will be of great value.

There are two useful indexes, one for authors and one for subjects, in accordance with the custom of certain editors, though one index in a single alphabet is far to be preferred. The illustrations are well chosen, and the paper and type worthy of the firm that has done so much to advance science by placing valuable books in the hands of teachers and pupils.

H. C. B.

CORRESPONDENCE.

THE INTERACTION OF MAGNESIUM AND SOLUTION OF SULPHATE OF COPPER.

To the Editor of the Chemical News.

Sir,—In a communication to the Chemical Society, on the 3rd inst., Dr. Divers disputes the suggestion of Prof. Clowes, that it is the combined action of magnesium and copper sulphate in water that causes the evolution of hydrogen gas when these substances are brought together. He lays especial stress on copper sulphate being an acid salt, and capable of being decomposed into sulphuric acid and a basic sulphate.

I have made lately a large number of experiments on the action of magnesium on metallic salts, and some of my results point distinctly in favour of Clowes and Caven's theory. For instance, if magnesium is placed in a cold strong solution of either sodium chloride, calcium chloride, or calcium nitrate, a copious evolution of hydrogen takes place, and the solutions become distinctly alkaline to litmus or phenolphthalein. A white solid residue is left in each case, consisting in the case of calcium chloride at least of both Mg and Ca oxides. With the calcium salts sufficient Mg is taken into solution to give a distinct precipitate with the ordinary reagents; I have not been able to obtain a precipitate from the solution of NaCl, which simply shows that MgO is no more soluble in NaCl than in pure water.

These are all neutral salts, and yet their solutions are decomposed by magnesium in the cold. Ammonium salts, such as the chloride and nitrate, give a similar reaction, but, as is well known, ammonic hydrate alone has the same action on this metal.—I am, &c.,

E. G. Bryant.

King's School, Pontefract,
March 20, 1898.

On Hydrocinnamide.—Marcel Delepine.—Hydrocinnamide crystallises with half a molecule of water, and has the fundamental properties of the glyoxalidines; it is a base, giving salts undecomposable by acids; the body $C_{54}H_{51}N_5$ does not exist. The author thinks the name *cinnamine* would be more appropriate.—*Comptes Rendus*, cxxvi., No. 9.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 8, February 21, 1898.

Chemical Actions brought about by the Electric Discharge. (Methods).—M. Berthelot.—The author has paid particular attention to the fixation of nitrogen by the organic compounds under these conditions, and his experiments are now complete on 120 systems. The general arrangement of the experiments was to place the substance to be operated upon in a narrow tube of convenient shape, in such a position that it must play the part of a dielectric, and be incessantly traversed by the discharges of a high tension apparatus such as a Ruhmkorff coil, fitted with a Leyden jar and a Marcel Deprez interrupter, giving many hundreds of interruptions a second. The reactions studied were between gases, liquids, and solids, the conditions being varied in the case of each one. Carbides of hydrogen and the compounds containing little oxygen gave first a little acetylene, but this soon disappeared. Compounds containing much hydrogen, such as formene, when in the presence of nitrogen, first gave ammonia, but this also soon disappeared, and it often happened that large volumes of gas were first produced, which were eventually re-absorbed by reason of fresh reactions. In general the nitrogen fixed under the prolonged influence of the electric discharge appears to exist as an ammoniacal derivative, such as an amide or amine, but especially as a polyamine.

Chemical Action exercised by the Electric Discharge on Organic Compounds. (Gaseous Systems; Carbides of Hydrogen and Nitrogen).—M. Berthelot.—A long paper, in which the author gives the results of a large number of experiments by the above-mentioned method on formene, CH_4; hydride of ethylene, C_2H_6; ethylene, C_2H_4; acetylene, C_2H_2; propylene, C_3H_6; trimethylene, C_3H_6; and acetylene, C_3H_4.

The Derivatives of Cinchonine.—E. Grimaux.—As a starting point the author took the bromised compound obtained by treating the raw product from the oxidation of cinchonine, or of quinine by bromine, and obtained $C_9H_{14}BrNO_2,HBr$. By treating this with picric acid he obtained a picrate of bromomezoquinene; this can be dissolved in strong potash on the water-bath, and on cooling a deposit of crystalline plates is obtained. He also obtained acetyl-mezoquinene and oxymezoquinene.

On a Combination of Phosphoric Anhydride and Benzene.—H. Giran.—Already inserted.

Ktypeite, a New Form of Carbonate of Lime, different from Calcite and Arragonite.—A. Lacroix.—This new mineral constitutes exclusively the pisolites from the thermal springs of Carlsbad and Hammam-Mescoutine, often described as having been formed from arragonite. When heated in a glass tube these crystals first of all decrepitate at a dull red heat and then detonate with violence, often shattering the glass. Ktypeite evidently exists under conditions of extreme tension, for after having been tapped with a hammer, though not sufficiently hard as to break the crystals, but only to disintegrate them, it can be heated to redness without detonating. This extreme state of tension is also shown by its action with parallel polarised light. Its density is from 2·58 to 2·70, that of calcite being 2·71.

No. 9, February 28, 1898.

Chemical Actions of the Electric Discharge. (Oxides of Carbon and Nitrogen; Gaseous Systems).—M. Berthelot.—In the present memoir the author commences with the binary compounds, such as carbonic acid and carbonic oxide; he then goes on to the study of the ternary compounds, alcohols and ethers, aldehyds and acids. The paper, however, is a very long one and not suitable for abstraction.

Properties and Crystallisation of Anhydrous Sulphide of Barium.—A. Mourlot.—Sulphide of barium was prepared by means of the electric furnace; first the pure amorphous sulphide was produced by the action of sulphuretted hydrogen on the carbonate at a red heat, taking care to substitute hydrogen for the former gas towards end of the experiment; the density of this sulphide, taken in benzine at 15°, is 4·30 when powdered and 3·95 in large fragments. Analyses give its composition as:—

		Theory.
Ba..	81·5	81·09
S	18·03	18·91

Sulphate of barium was then intimately mixed with the necessary amount of carbon, and after heating strongly in the electric furnace for four minutes, a mass was obtained which showed a distinct crystalline formation in the interior. Analyses showed it to be:—

			Theory.
Ba	81·20	81·29	81·09
S	18·65	18·30	18·91

Its density is practically the same as the former product. It crystallises in white crystals, colourless when seen in thin layers, but black when thicker, owing to the presence of carbon. They have two very distinct cleavage planes, at right angles, and have no action on polarised light. The hardness of crystallised sulphide of barium is not great, as it will not scratch glass. It is readily attacked by fluorine, with incandescence, as well as by chlorate of potassium and oxide of lead in the same manner. Phosphoric anhydride and oxychloride of phosphorus reduce it with incandescence, forming a reddish body.

Action of Carbonic Oxide on Palladous Chloride.—E. Fink.—Palladous chloride is heated to about 260° in a glass tube, and a current of dry carbonic oxide passed over it; after some time the cool part of the tube becomes coated with a reddish substance near the furnace and yellow in the cooler parts of the tube; this substance can only contain palladium, chlorine, and carbon, and it is shown that it consists of a mixture in variable proportions. The analysis of the yellow crystals gives the formula—

$$C_3O_3 - Pd_2Cl_4 \text{ or } PdCl_2{<}^{CO-PdCl_2}_{CO-CO}{>}PdCl_2,$$

decomposable by water; heated to 263° it loses carbonic oxide and forms a new compound corresponding to the formula $COPdCl_2$ or $CO{=}{=}PdCl_2$.

On an Oxyptomaine.—O. de Coninck.—The manner of formation of the new compound described in this note, together with its properties and its reactions, show it to be an oxycollidine, $C_8H_{10}(OH)N$, a higher homologue of the oxypyridines already described by the same author; the name *collidone* is proposed. This one appears to be the first known.

Zeitschrift fur Analytische Chemie.
Vol. xxxvii., No. 1.

Estimation of Carbon and Hydrogen by Combustion in Vacuo. — K. A. H. Mörner. — The principle of this method is the same as that of Klingeman. The substance (0·08—0·12 grm.) is mixed with powdered copper oxide and asbestos fibres, and placed in a tube closed at one end; the tube is nearly filled up with granular copper oxide. The tube is then placed in the channel of a water-bath, and connected with a mercury-pump. During the pumping, the water surrounding the tube is heated to boiling-point, so that any water inside the tube may vapourise and the pumping be made easier. When the tube is exhausted, the other end is closed, the tube placed in the furnace, and the combustion proceeds in the ordinary

way. The products of combustion are collected in a eudiometer and analysed.

A New Method of Estimating Grape Sugar and Milk Sugar.—E. Riegler.—The sugar solution is treated with Fehling's solution; the copper is estimated, before and after the reduction, by iodine, according to de Haen's method. Before milk sugars can be estimated, all albuminous substances must be removed by asaprol. To do this 15 c.c. of asaprol and citric acid solution are put, together with 10 c.c. of milk solution, into a 100 c.c. flask, which is then filled up to the mark with water. The liquid is well shaken, warmed to 60°, and filtered. The sugar can then be estimated by taking 20 c.c. of this sugar solution free from albuminous matter, and 20 c.c. of Fehling's solution, and boiling for about six minutes. In the experiment described the reduced copper amounted to about 100 m.grms., and 1 m.grm. Cu corresponds to 0·725 m.grm. of milk sugar.

Research on the Composition of Acid Thorium Oxalates.—Carl Glaser.—A thorium earth was brought into solution by treating it with H_2SO_4, and after filtration the thorium was precipitated by oxalic acid. After careful washing, the oxalate was boiled with excess of strong ammonium oxalate solution, until it dissolved; after cooling it was filtered, and the double salt decomposed by acid. To determine what was the influence of the temperature on the reaction, three experiments were made, which gave nearly coincident results (51 per cent ThO_2). On leaving the precipitate for a long time in contact with the acid, there was a slightly higher yield (52·57 per cent ThO_2). The estimation of the oxalic acid and water was conducted in the ordinary way, and the formula found to be either $Th_5H_4(C_2O_4)_{12}+25H_2O$ or $Th_2H_2(C_2O_4)_5+9H_2O$.

A Small Spirit-flask. — Jos. Loczka. — The flask is drawn and described.

An Evaporating Funnel.—D. S. Bosnjakovic.—This vessel can be used both as an evaporating basin and a filter, and so it prevents the necessity of transferring a precipitate from an evaporating basin to the filter. Two diagrams are given showing the position of the funnel in its two uses.

Estimation of Chromium in Chrome-iron Ore.—H. Fresenius and H. Bayerlein.—A weighed quantity of finely-powdered ore is digested in a 300 c.c. flask with 50 c.c. of concentrated HCl, at first in the cold, and as soon as the evolution of gas ceases it is gently warmed, until a very slight insoluble residue remains. The liquid and the residue are placed in a basin and evaporated to dryness. Silicates are then removed with HCl and water, and the liquid is filtered. The dark coloured residue is fused in a silver crucible with Na_2O_2, and then treated with water and the yellow solution filtered. There remains on the filter-paper a black residue, insoluble in HNO_3. The solution is treated with HCl to precipitate any silver, and the filtrate concentrated by evaporation. The residue is now treated with a little HCl and water, and again excess of Na_2O_2 is added, by which some iron precipitate is obtained free from chromium. To free the solution from excess of acid, it is placed in a 500 c.c. flask, together with the solution obtained from the first fusion with Na_2O_2; excess of Na_2O_2 is added, and the solution shaken and warmed, until the evolved gas ceases to come off. It is filtered, and the iron precipitate obtained, after washing, is dissolved in HCl. The solution is again concentrated by evaporation, added to the residue, and once again treated with Na_2O_2. By this method the iron precipitate is always free from chromium. To separate the chromium from its strong alkaline solution it must be concentrated, and then carefully neutralised with HCl, and H_2O_2 added until the slight blue colour of the solution is changed to green on warming. The solution is now boiled, the H_2O_2 decomposing, and the liquid evaporated to dryness. The residue is treated with HCl, and the chromium will come down with ammonia free from silicates. If the chromium oxide obtained is not a pure product, it can be fused with soda and saltpetre, treated with water, and the aqueous solution decomposed with ammonia and ammonium carbonate.

Journal de Pharmacie et de Chimie,
Series 6, vol. vii., No. 4.

Action of Iodine on Antipyrine. Application to the Estimation of Antipyrine and of Iodine. — J. Bougault. — The author has made a certain number of experiments, with the object of determining the conditions under which the absorption of iodine by antipyrine takes place, and he arrives at the conclusion that the reaction which takes place in alcoholic solution is such that one molecule of antipyrine used corresponds very exactly with one molecule of iodine. If to 20 c.c. of a solution of antipyrine (1 grm. per 100 c.c. of alcohol we add 20 c.c. of a solution of bichloride of mercury (2·5 grms. per 100 c.c. of alcohol), and then, drop by drop, a solution of iodine (at 1·351 grms. per 100 c.c. of alcohol) until the appearance of a persistent faint yellow colour, showing an excess of iodine, the number of c.c. of iodine used, multiplied by 5, will give the number of grms. per cent of pure antipyrine in the sample under examination. Inversely the amount of iodine present in any sample can easily be estimated.

The Estimation of the Phospho-glycerates. — MM. Adrian and Trillat.—When we add sulphuric acid of a known strength to a cold aqueous solution of a neutral phospho-glycerate of an alkaline earth, and use heliantine as an indicator, the indication appears from the moment that a half molecule of acid has been added for one molecule of the neutral salt. This fact shows that sulphuric acid transforms the neutral phospho-glycerate into an acid salt, and that the latter is not decomposed by the sulphuric acid,—at any rate not in the cold.

Volumetric Estimation of Combined Sulphuric Acid.—F. Telle.—As a modification of previous processes, the author proposes to estimate the excess of chromate by titrating, by means of hyposulphate, the iodine which is displaced, in hydrochloric solution. Two solutions of equal strengths, of chloride of barium and bichromate of potassium, are used. The sulphuric acid is precipitated by the chloride of barium after acidulating with HCl. The excess of baryta is then precipitated by the bichromate of potassium in slightly alkaline solution, and, finally, the excess of chromate is estimated by the iodine displaced by the hyposulphite.

MISCELLANEOUS.

Royal Institution. — The following are the Lecture Arrangements after Easter: — Mr. T. C. Gotch, two lectures on "Phases of Art, Past and Present"; Dr. S. R. Gardiner, four lectures on "The Historical Development of Europe"; Professor S. H. Butcher, two lectures on "Literary Criticism in Greece"; The Rev. Canon Ainger, three lectures on "Some Leaders in the Poetic Revival of 1760 to 1820—Cowper, Burns, and Scott"; The Right Hon. Lord Rayleigh, F.R.S., three lectures on "Natural Philosophy"; Dr. E. E. Klein, two lectures on "Modern Methods and their Achievements in Bacteriology"; Sir Walter Parratt, four lectures on "Programme Music" (with musical illustrations); Mr. J. A. Thomson, two lectures on "The Biology of Spring"; Dr. R. Caton, two lectures on "The Temples and Ritual of Asklepios at Epidaurus and Athens." The Friday evening meetings of the members will be resumed on April 22nd, when Mr. W. H. M. Christie, the Astronomer Royal, will deliver a discourse on "The Recent Eclipse." Succeeding discourses will probably be given by Prof. A. Gray, Mr. E. A. Minchin, Prof. W. A. Tilden, The Right Hon. D. H. Madden, Lieut.-General The Hon. Sir A. Clarke, Prof. W. M. Flinders Petrie, The Right Hon. Lord Rayleigh, and other gentlemen.

Chemical Actions of the Electric Discharge. (Alcohols and Derived Ethers in the presence of Nitrogen.—M. Berthelot.—In this paper the author describes the reactions of the electric discharge on the methylic, ethylic, normal- and iso-propylic and allylic alcohols, the reactions being carried to their extreme limits; he also includes experiments on various phenols as well at others with alcoholic compounds formed by dehydration, such as a simple ether, glycolic ether or pseudoxide of ethylene, and the dialcoholic ethers. The results of these experiments are all given at great length.—*Comptes Rendus*, cxxvi., No. 9.

Corundum Deposits in Eastern Ontario. — Until about thirty years ago the only sources of corundum were a few river washings in India and elsewhere, where it occurred in scattered crystals. In 1869 it was found by Mr. W. P. Thompson in Northern Georgia, U.S.A.; but late in 1896 Mr. Ferrier, of the Geological Survey, made a discovery of corundum in the northern part of Carlow Township, Hastings County, Canada. He made careful examination of the occurrence of the ore, and, taking back with him to Ottawa a lot of samples, he reported his discovery to Dr. Geo. M. Dawson, Director of the Survey. Dr. Dawson, in turn, reported it to the Bureau of Mines here, and as the mineral was on Crown lands the Commissioner of the Lands Department withdrew from sale a large block in the vicinity pending a more careful exploration. A quantity of the ore was taken out under his instructions, and samples were distributed to prospectors and others in the eastern part of the province. The result was that several other discoveries were soon reported, and early last summer Mr. W. G. Miller, of the Kingston School of Mining, was employed to make a thorough exploration of the country. He spent ten weeks in the northern part of Hastings and the southern part of Renfrew, and succeeded in tracing the corundum belt for a distance of 30 miles across country from Carlow in the west to Sebastopol in the east. The mineral was found in place in seven different townships,—Carlow, Bangor, Raglan, Radcliffe, Brudenell, Lynedoch, and Sebastopol,—over an area of about 100 square miles. There are indications, however, that the belt extends far north-eastward into Renfrew, as float boulders have been discovered at several points beyond the eastern end of the explored belt. If it turns out, as appears almost certain, that the corundum can be smelted economically for the production of aluminium, this alone will give it a value second in importance to none other in the province. A sample of the ore containing tin, as well as numerous samples of corundum, have been placed in the collection of minerals in the Parliament Buildings, Canada, where they are attracting considerable attention.

MEETINGS FOR THE WEEK.

Monday, 28th.—Society of Arts, 8. (Cantor Lectures). "The Thermo-chemistry of the Bessemer Process," by Prof. W. N. Hartley, F.R.S.

Tuesday, 29th.—Royal Institution, 3. "The Simplest Living Things," by Prof. E. Ray Lankester, M.A., LLD., F.R.S.

—— Society of Arts, 8. "English Art in Illuminated MSS.," by Sir Edward Maunde Thompson, K.C.B., D.C.L.

Wednesday, 30th.—Society of Arts, 8. "Telegraphy Across Space," by Professor Silvanus P. Thompson, F.R.S.

—— Microscopical, 8. Exhibition of Mounted Rotifers, by C. F. Rousselet.

Thursday, 31st.—Royal Institution, 3. "Recent Researches in Magnetism and Diamagnetism," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.

—— Chemical, 3. Annual General Meeting.

—— Society of Arts, 4.30. "The Earthquake in Assam," by Henry Luttman-Johnson, I.C.S.

Friday, April 1st.—Royal Institution, 9. "Liquid Air as an Analytic Agent," by Professor Dewar, F.R.S.

Saturday, 2nd.—Royal Institution, 3. "Portraits as Historical Documents," by Lionel Cust, M.A., F.S.A.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Indicators.—Can any reader tell me of another indicator which may be used in place of ferricyanide in the estimation of phosphorus by uranium acetate? I wish to apply this method to estimating phosphorus in pig-iron and steel, and of course the iron will render ferricyanide useless.—V. G. J.

Products of the Distillation of Wood.—I am desirous of procuring some information in regard to manufacture and chemical analysis of the products resulting from the destructive distillation of wood, such as wood alcohol, acetate of lime, &c. In other words, information pertaining to running a chemical plant, manufacturing wood alcohol and making charcoal to the best advantage. Some good book on the above, if there is one, is what I would like. Any information on this subject will be gratefully received and appreciated.—E. E. J.

WILLIAM F. CLAY,
Chemical & Technical Bookseller
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Wanted—Any Vols. or Nos. of the *Journal of the Society of Chem Industry*, 1882-86, *The Journal of the Chemical Society*, 1849-80. *The Analyst*, *Journal of Iron and Steel Inst.*, 1869-80. *Proc. of the Royal & Phys. Socs. of Edin.*, Gmelin's "Chemistry," vl. 19 (Index). Graham's "Physical Researches," and any Standard Literature.

WILLIAM F. CLAY, Bookseller, 18, Teviot Place, Edinburgh.

COUNTY BOROUGH of WEST HAM.

The COUNCIL of the Borough hereby invite APPLICATIONS from duly qualified persons for the following position on the Teaching Staff of the TECHNICAL INSTITUTE now in course of erection:—

HEAD OF THE CHEMICAL DEPARTMENT.

Full particulars of the duties attached to the post and of the salary to be paid may be obtained on application to the Principal of the Technical Institute, Town Hall, West Ham, E., before March 31st.

By order of the Council,
FRED. E. HILLEARY,
Town Clerk.

Town Hall, West Ham, E.,
March 16th, 1898.

JAMES HICKISSON, otherwise HICHISSON (trading as John Bond), deceased.

NOTICE pursuant to Statute 22 and 23 Victoria, chapter 35, is hereby given, that all persons having any claim or demand against the Estate of the late JAMES HICKISSON, otherwise HICHISSON, of Erleigh, Gordon Road, Bournemouth, in the county of Southampton, formerly of Wilton, Drummond Road, Bournemouth, aforesaid, who carried on business at 75, Southgate Road, London, N., as a Marking Ink and Rubber Stamp Manufacturer, and who died on the 29th September, 1897, and whose Will and Codicils were proved by John James Rorie Friend and Duncan Watts, two of the Executors, on the 15th December, 1897, in the Principal Registry, are required to send particulars in writing of such claims or demands to the undersigned before the 23rd day of April, 1898, after which date the Executors will distribute the assets among the persons entitled, having regard only to the claims of which they shall then have had notice.

Dated this 23rd March, 1898.

LESLIE & HARDY,
Solicitors to the said Executors.

17, Bedford Row,
London, W.C.

THE CHEMICAL NEWS.

Vol. LXXVII., No. 2001.

ON THE CONNECTION BETWEEN THE ELECTRICAL PROPERTIES AND THE CHEMICAL COMPOSITION OF DIFFERENT KINDS OF GLASS.*

By Professor ANDREW GRAY, LL.D., F.R.S.,
and
Professor J. J. DOBBIE, M.A., D.Sc.

The experiments and results described in the following paper are a first instalment of work we have undertaken with a view to determining, if possible, the circumstances which affect the conductivity and specific inductive capacity of glass. It appeared from some experiments, which were carried out by Professor T. Gray and ourselves some years ago (*Roy. Soc. Proc.*, No. 231, 1884) that it might be of interest to have a number of glasses specially made up with a view to testing some of the conclusions then arrived at.

A result previously obtained by Professor T. Gray had shown that potash and soda-lime glasses have a higher conductivity than flint glasses; this result had also been arrived at by Dr. Hopkinson. In particular it seemed desirable to ascertain whether by increasing the amount of lead oxide and diminishing the amount of soda, the conductivity would go on diminishing. We have experienced great difficulty in getting glasses made according to our own specifications. We endeavoured to make the glasses ourselves, and several experiments were made accordingly, both in the laboratories here and at the Ogwen Tile Works, where a large furnace had been erected for the construction of tiles from slate dust. Some success was achieved, but it was found impossible, without the expenditure of far more time than could be spared, to obtain the glasses in a condition suitable for the experiments we wished to carry out.

Through the kindness, however, of Messrs. Schott and Co., of Jena, and of Messrs. Powell and Sons, Whitefriars, London, we have recently obtained a number of specimens of glass all richer in lead than the specimens formerly available, and, further, in some cases, practically free from soda. We have also had made to order by Messrs. Schott specimens of their own glass, used, we believe, chiefly in the construction of thermometers, as well as of a barium crown-glass, which have not hitherto, so far as we are aware, been experimented with.

Determination of Conductivity.—The method of experimenting followed was practically the same as that described in the paper already referred to, but its nature may perhaps here be indicated.

Owing to the large percentage of lead oxide in some of the glasses prepared for us by Messrs. Schott, it was found impossible to blow them into flasks, and they were therefore cast into plates; the arrangements therefore required some modification for their case.

The specimens which were in the form of flasks were filled up with mercury to the bottom of the stem (which in most cases was about 8 or 9 inches long), and the flask thus filled was sunk in a bath also containing mercury, so that the mercury was at the same level inside and outside. One terminal of a circuit containing a battery of about thirty secondary cells and a very sensitive galvanometer was connected to the mercury within the flask by a wire passing down the neck, while the other terminal was connected to the mercury in the bath.

The galvanometer was the instrument formerly used and described in *Roy. Soc. Proc.*, vol. xxxvi., p. 287. It was carefully insulated, as was also the reversing key, and all necessary precautions were taken to make sure that the current passing through the galvanometer was that passing through the walls of the flask between the mercury coatings. Thus it was always verified that no deflection took place when the wire was withdrawn from the flask and placed round the outside of the neck. The bath could be heated to any temperature required in the experiments.

The conductivity was calculated from the dimensions of the flask and the thickness of its walls, as described in the former paper.

In the capacity measurements the plate or flask, as the case might be, was supported as described above. A quadrant electrometer was kept connected to the plates of one of Lord Kelvin's air leydens. This was charged with twelve secondary cells, and therefore to a difference of potential of about 24 volts. After the battery had been removed a reading was taken of the electrometer deflection, and then the specimen was connected for a very short interval of time as a condenser in parallel with the leyden.

This connection was made by means of a myrograph pendulum which, when freed, swung over a considerable arc to a catch which prevented it from returning. At its lowest point a metal piece projecting below the bob touched the top of a tongue projecting upwards from a hinge at its lower end, and leaning against the point of an adjustable screw. The connection between the two condensers thus only endured while the three pieces, the screw, tongue, and bob, were in contact. This was only the interval of time required for a pulse of flexure to travel about a centimetre in a bar of steel about half a centimetre thick and about a centimetre broad. The interval was reckoned as at most about 1/30,000 of a second.

The plates were originally rather over a quarter of an inch thick, and after some observations of capacity had been made on some of them, and it had appeared that their resistance was too great to be measurable, they were cut down on a turning-table used for cutting slates, to a thickness of about 3 m.m.; they were then fixed on a bed of pitch, and ground down by hand to a thickness of about 0·24 c.m. They were polished and properly cleaned, and then covered on both sides with a dense and thoroughly adherent coating of silver. This was cut away for a space of about half an inch round the edges. Great care was taken to remove every trace of silver, and to make the edge thoroughly clean.

While being experimented on the glass plate was laid with one coating of silver resting on a plate of copper at the bottom of an iron bath. Another plate of copper was laid on the upper coating of silver, and kept down with a weight, and the connections of the battery circuit, described above, were made with the copper plates. The iron bath was placed within a larger bath partly filled with sand, so that the temperature could be raised by heating the outer bath from below.

The results of the experiments are exhibited in the accompanying table. We have there given the density, specific resistance, specific inductive capacity, and chemical composition of each specimen experimented on.

The resistance was taken after five minutes' electrification in each case. The "Jena" glass (XXIV. of the table), in both resistance and capacity experiments, showed very considerable polarisation effects, which were a very long time in disappearing, though the conducting coatings of the flask were kept short-circuited. The polarisation of the lead glass made by Messrs. Powell was also considerable.

On the other hand, it is very remarkable that the barium glasses XXIII., in the capacity experiments, showed little or no sign of polarisation effects; and we propose to make some further investigations of the physical properties of this glass.

* A Paper read before the Royal Society, February 17th, 1898.

CHEMICAL COMPOSITION.

No.	Description of glass.	Density.	Specific resistance (ohms).	Specific inductive capacity.	Silica.	Lead oxide.	Ferric oxide and alumina.	Manganese monoxide and arsenious oxide.	Potassium oxide.	Sodium oxide.	Total percentage.	Remarks.
XXI.	Lead potash glass made by Messrs. Powell and Sons, London.	3·495	Too high to measure, certainly above $18{,}000 \times 10^{10}$ at 130° C.	7·966 at 15° C. 7·630 at 120° C.	50·5	42·14	0·41	—	6·93	trace	99·98	Absorption effects in electrical experiments very marked.
XXII.	Lead potash glass made by Messrs. Schott and Co., Jena.	3·591	Too high to measure, certainly above $35{,}000 \times 10^{10}$ at all temperatures to 135° C.	7·991 at 14° C.	44·5	46 6	trace	0·4	8·0	0·5	100·0	Absorption effect slight.

No.	Description of glass.	Density.	Specific resistance (ohms).	Specific inductive capacity.	Silica.	Boron trioxide.	Alumina.	Manganese monoxide and arsenious oxide.	Zinc oxide.	Barium oxide.	Magnesia.	Potassium oxide.	Sodium oxide.	Total percentage.	Remarks.
XXIII.	Barium glass made by Messrs. Schott and Co., Jena.	3·565	Too high to measure, certainly above $59{,}000 \times 10^{10}$ at all temperatures to 140° C.	8·5. No variation with temperature. No absorption effect.	33·0	12·0	6·0	1·0	—	48·0	—	trace	trace	100·0	This glass showed no trace of polarisation.
XXIV.	Zinc soda 'Jena glass' made by Messrs. Schott and Co.*	3·493	$596{\cdot}5 \times 10^{10}$ at 43° C. $0{\cdot}200 \times 10^{10}$ at 140° C.	7·54 at 15° C. Conduction too great at high temperatures.	67·6	8·0	trace	0·4	9·0	—	5·0	—	10·0	100·0	Considerable absorption effects.

Dimensions of Specimens.

XXI. Flask.

Internal radius.. .. 3·741 c.m.
External „ .. .. 3·522 „
Effective surface .. 174·921 sq. c.m.

XXII. Plate.

Length of silvered surface 12·81 c.m.
Breadth of ditto. .. .. 11·90 „
Area .. .. 152·439 sq. c.m.
Mean thickness .. .. 0·24 c.m.

XXIII. Plate.

Length of silvered surface 18·8 c.m.
Breadth of ditto. .. .. 14·31 „
Area .. .. 269·028 sq. c.m.
Mean thickness .. .. 0·235 c.m.

XXIV. Flask.

Effective area . .. 209·2 sq. c.m.
Mean thickness .. 0·935 c.m.

* Experiments were made with four different flasks of this glass, with results fairly represented by those given in table. The factor of diminution of resistance for a rise of temperature of 20° C. was about one-fifth.

{Chemical News, April 1, 1898.

In our previous paper, the results obtained with eight different samples of lead glass were compared, and it was shown that the electrical conductivity fell off almost quite regularly as the amount of lead oxide increased, and increased with an increase in the amount of soda. The glass which possessed the highest specific resistance (8400×10^{10} ohms) contained 40·5 per cent of lead oxide, 7·5 per cent of potassium oxide, and 2·1 per cent of sodium oxide. Both of the lead glasses dealt with in this paper contained a still higher percentage of lead oxide, and were almost free from soda, and the electrical resistance was so great as not to be measurable. It is, of course, impossible to say how far this result is due to the increase of lead oxide, and how far to the elimination of soda. With the view of definitely settling this point, Messrs. Powell and Sons have kindly undertaken to prepare for us a glass exactly similar to XXI., but having the potash replaced as nearly as possible by the equivalent amount of soda. It should be noticed that the amount of foreign matter (*i.e.*, of ingredients other than silica, lead oxide, and alkali) present in glasses XXI. and XXII. is very small, and is less than one-fourth of the amount present in the purest glass previously tested, which was also, it may be mentioned, the glass possessing the highest resistance.

It is noteworthy that the barium glass XXIII. has a very high resistance, and in this respect behaves more like lead than lime glasses, which have usually a low resistance. It is impossible, however, in view of the somewhat complicated composition of this glass, to say how far the high resistance is due to the presence of the barium, and how far it may be influenced by other ingredients, especially the boric acid, which was not present in any of the glasses previously examined by ourselves or others.

The "Jena" glass XXIV. has a low resistance, as was to be anticipated from its high percentage of soda and complex composition.

The chemical composition of glass XXI. is capable of being expressed with tolerable accuracy by a simple chemical formula, and this is also in accord with previous experience, which pointed to the conclusion that a glass, which approaches in composition to a definite chemical compound, has a high resistance.

Our knowledge of the chemistry of glasses is still very imperfect, and we cannot say in what way the silica is distributed amongst the bases. We give, therefore, merely the relative number of formula weights of each oxide present, calculated from the analytical numbers, after allowing for the elimination of traces of foreign matter.

Specimen XXI.

After allowing for traces of iron and alumina, the composition of this glass may be expressed by the formula—

$$22SiO_2,5PbO,2K_2O,$$

or—

$$5(PbO,2SiO_2)+2(K_2O,6SiO_2).$$

	Found.	Calculated.
SiO_2	50·72	50·53
PbO	42·32	42·33
K_2O	6·96	7·13
	100·00	99·99

Specimen XXII.

This glass is essentially a lead-potash glass mixed with a very small quantity of lead-soda glass. Allowing for the small quantity of manganese oxide, arsenious oxide, and other impurities present, we obtain as the simplest expression for the composition of this glass in terms of the formula weights of the oxides present:—

$$184SiO_2,52PbO,21K_2O,2Na_2O.$$

	Found.	Calculated.
SiO_2	44·67	44·84
PbO	46·78	46·71
K_2O	8·03	7·95
Na_2O	0·50	0·49
	99·98	99·99

If we eliminate the soda and a corresponding quantity of silica, calculated on the assumption that each formula weight of soda is in combination with three of silica, we obtain as an expression for the composition of the lead-potash glass—

$$17SiO_2,5PbO,2K_2O.$$

	Found.	Calculated.
SiO_2	44·07	44·11
PbO	47·72	47·82
K_2O	8·19	8·06
	99·98	99·99

Specimen XXIII.

This is a borosilicate of barium and alumina. After allowing for the small quantities of arsenious oxide and manganese oxide which it contains, it has the composition—

$$28SiO_2,16BaO,3Al_2O_39B_2O_3.$$

	Found.	Calculated.
SiO_2	33·33	33·35
BaO	48·48	48·20
Al_2O_3	6·06	6·02
B_2O_3	12·12	12·40
	99·99	99·97

Specimen XXIV.

The "Jena" glass is essentially a borosilicate of zinc, soda, and magnesia, containing—

$$20SiO_2,2ZnO,2MgO,3Na_2O,2B_2O_3.$$

	Found.	Calculated.
SiO_2	67·87	68·05
ZnO	9·03	9·11
Na_2O	10·04	10·46
MgO	5·02	4·50
B_2O_3	8·03	7·87
	99·99	99·99

ON THE OCCURRENCE AND EXTRACTION OF THORITE, MONAZITE, AND ZIRCON.*

By P. TRUCHOT.

(Concluded from p. 135).

As monazite constitutes only a minute portion of the mother-rock it is not, as a rule, practicable to treat it directly. Still some attempts have been made on the sides of the hills, amongst others the Pheifer mine in Cleveland county, 2 miles north-east of Shelby. The rock is a coarse mica (muscovite and biotite), and the crystals of monazite disseminated throughout it can be plainly seen with a lens. It is very little decomposed, and is still hard. The soil and the subsoil are worked for monazite to a depth of 1·2 to 1·8 metres.

The gravel found is placed in trucks and run to the sluice-boxes. As Mr. Nitze pointed out, when the rock contains gold, monazite constitutes a very valuable by-product.

* *Revue Générale des Sciences*, No. 4, February 28, 1898.

TABLE II.—*Average Composition of Monazite and of Monazite Sands.*

	Formulæ.	Samples of Monazite.							Monazite Sands.		
		Mount Ilmen.	Antioquia, New Granada.	Cara-vellas, Brazil.	Burke County, N. Carolina.	Amelia County, Virginia.	Ottawa County, Canada.	Burke County, N. Carolina.	Shelby, North Carolina.	Bellewood, North Carolina.
Phosphoric anhydride	P_2O_5	27·32	19·13	28·70	29·28	26·12	26·86	18·38	28·16	26·05
Oxide of cerium	Ce_2O_3	31·31	22·88	31·30	31·38	29·89	24·84	32·93 (CeO)		
Oxide of lanthanum	La_2O_3	31·86	14·69	24·50					63·80	59·09
Oxide of didymium	Di_2O_3	—	—		30·88	26·66	26·41	7·93		
Oxide of yttrium	Y_2O_3	0·52	1·71		—	—	4·76	—	—	—
Oxide of thorium	ThO_2	5·55	16·64		6·49	14·23	12·60	1·43	2·32	1·19
Silica	SiO_2	1·37	9·67		1·40	2·85	0·91	6·40	3·20	1·45
Alumina	Al_2O_3	0·13	2·90					1·62		0·15
Sesquioxide of iron	Fe_2O_3	0·26	—				1·07	—	—	—
Protoxide of iron	FeO		3·56					7·83		
Protoxide of manganese	MnO		4·89					—	traces	0·65
Lime	CaO	0·55	1·25				1·54	1·20		
Magnesia	MgO	—	0·40				0·04	—	—	—
Oxide of zirconium	ZrO_2							13·98 ($+Y_2O_3$)	1·52 ($+Y_2O_3$)	2·68 ($+Y_2O_3$)
Oxide of tin	SnO_2	0·95	0·40					—	—	—
Oxide of lead	PbO							traces		
Fluorine	F									
Tantalic acid	Ta_2O_5							—		
Titanic acid	TiO_2							0·66		6·39
Water	H_2O	0·41	0·71		0·20	0·67	0·78	4·67	0·61	1·40
		—	—		—	—	—	—	—	—

Monazite is thus localised in the west of North Carolina, where the sands richest in thorium are found, in the counties of Burke, Cleveland, McDowell, and the neighbourhood of Bellewood and Carpenter's Knob.

2. *The Deposits of Idaho.*—Last year in the Idaho water-shed, at about 30 miles N.N.E. of Boise city, a large deposit of monazite was discovered, also forming one of the original constituents of the Idaho granite. Certain samples of the sands from the lakes of Idaho City have given, after washing, a monazite sand containing up to 70 per cent of monazite, mixed with zircon, ilmenite, &c.

The alluvial gold washings at Wolf Creek, near Placerville, have also yielded large quantities of monazite, mixed with rutile, garnet, &c.

3. *The Canadian Deposits.*—Monazite has been discovered and worked in Canada, at the Villeneuve mine in the county of Ottawa, mixed with mica, garnet, tourmaline, &c.

Deposits in Brazil, Columbia, and the Argentine Republic.

Monazite sands have been found in important deposits in several provinces of Brazil, where they were discovered by M. Gorceix, Director of the School of Mines at Ouro-Preto; in the province of Bahia, at Salabra and at Caravellas; in the province of Minas Geraes, at Diamantina; and in the provinces of Goyaz, Cuyaba, San Paulo, and Rio de Janeiro.

The most considerable deposits in Brazil are found in the province of Bahia, in the form of sand-banks on the sea-shore, particularly at the southern extremity of this province, near the island of Alcobaca.

The continuous destruction of the rocks, by the waves of the sea, has led to a gradual concentration, and we thus find sands of a high average density containing a notable proportion of monazite. The sand is loaded directly on board ship, which enables it to be obtained at a relatively very low price, the actual handling being only the loading. This monazite sand contains an average of 4 or 5 per cent of oxide of thorium, and it almost exclusively supplies the European market.

The other Brazilian deposits have been found in the gold and diamond placer workings in the province of Minas Geraes, Cuyaba, and Goyaz. Monazite is there found in the form of nodular masses, stained and coloured with brilliant yellow particles of orangite. Monazite has been met with in the gold placers of Rio-Chico, at Antioquia, in the United States of Columbia; and in the sands of the Buenos Ayres River, in the Argentine Republic.

Table II. shows the average composition of monazite, and of the monazite sands, obtained from various deposits.

Table III. gives the quantity of oxide of thorium contained in a certain number of samples from North Carolina, analysed by Mr. Charles Baskerville. These analyses were carried out on commercial monazite sands containing about 67 per cent of monazite, the remainder being composed of quartz, garnet, zircon, and other minerals.

III.—*Zircon.*

Zircon, which is always found associated with monazite, and xenotime, &c., is a silicate of zirconium, with the formula ZrO_2SiO_4.

It crystallises in quadratic prisms, more or less well developed, and shows a large number of modifications. Sometimes they approach the rhomboidal type. Werner described this last variety as *hyacinth*, while the name *zircon* was restricted to the prismatic forms. It is also this latter form which has for many years been called Ceylon Jargon by lapidaries, after the name of the island which then supplied the most beautiful samples of zircons for use as jewels. Similarly to monazite, zircon crystallises in the primitive rocks—granite, syenite, biotite, &c. It possesses a brilliant lustre, is

TABLE III.—*Proportion of Thorium in Monazite Sands.*

	Oxide of thorium. Per cent.
1. Bennett's Mill, Silver Creek, Barber Co.	0·175
2. North-east Side, Brindle Ridge, Idaho ..	0·225
3. White Bank Gold Mine, Idaho..	2·15
4. Hall's Creek, at Morganton Road, crossing Idaho..	2·25
5. Bailey's Creek, 3 miles S.E. of Glen Alpine Station, Idaho	0·40
6. Linebacher Place, Silver Creek, Idaho ..	6·54
7. MacLewroth Place, Silver Creek, Idaho..	0·125
8. East part of Satterfield Creek, Idaho ..	0·29
9. MacLewroth Branch, MacDowell County	2·48
10. Bracket Town, South Muddy Creek, Idaho	0·26
11. Long Branch, Idaho	1·27
12. Alexander Branch, Idaho	6·30
13. David Peter's farm, Bellewood, Cleveland County	5·19
14. Proctor's farm, near Bellewood, Idaho ..	5·87
15. Wade MacCurd's farm, Carpenter's Knob, Idaho..	6·26
16. Tailings from No. 15	1·75
17. Henrietta, Rutherford County	1·93
18. Fallston, Cleveland County	3·40

transparent or translucent, and of a yellow, grey, brown, red, or hyacinth colour, and sometimes colourless.

Zircon is very widely distributed in Nature, and the most ancient known of its deposits are those of the Island of Ceylon and of Friedrichwarm in Norway, in the province of Christiania. Very beautiful samples are also found in the gemmiferous sands of Espally (Haute-Loire). It is also found at Miask (Ourel), and in the talcous schists of Pfitsch (Tyrol). Very important deposits have recently been discovered:—

1. In North Carolina and Colorado.
2. In Texas.
3. In New Zealand.

In North Carolina and Colorado the deposits of zircon are very much mixed up with those of monazite. It is the same with those of Idaho and Texas, of which we have spoken when on the subject of the monazite sands. But all the deposits are small when compared with that which was discovered last year in New Zealand.

This deposit, which covers a superficial area of 105 acres, is situated on the north-east side of Tasmania, half-way between Emin Bay and Circular Head. It is almost entirely composed of zircon, having a density of 4·7 and containing 63 to 64 per cent of oxide of zirconium, with variable quantities of lanthanum, didymium, thorium, niobium, erbium, cerium, and chromium.

It is in a gravel-bed, at about 20 or 30 c.m. below the surface, having a thickness of 20 c.m., that this deposit of zircon is found. It lies on a bed of blue clay of 60 c.m. in thickness, below which there is a bed of sand.

In its exploitation, which is in the hands of a Melbourne Company, large works have been already undertaken; up to the present the zircon is extracted simply by washing and trusting to the differences in density.

Table IV. shows the composition of zircon coming from different deposits.

TABLE IV.—*Average Composition of Zircons.*

	Formulæ.	Ceylon.	Norway.	El Paso, Colorado.	New Zealand.
Silica ..	SiO_2	33·85	33·61	29·70	33·50
Oxide of zirconium	ZrO_2	64·25	64·40	60·98	63·80
Protoxide of iron..	FeO	1·08	0·90	9·20	2·07
Magnesia	MgO	—	—	0·30	0·12

We see thus that the deposits of the rare earths tend to increase more and more, and we may easily prophecy that the industry of incandescent gas-lighting, which alone at present actually uses the rare oxides, can never use up the enormous amount of mineral which is now actually obtainable. It is no less true that—thanks to this industry, founded by Dr. Auer von Welsbach—Science has already benefitted by the numerous researches which have enabled us to determine, and partly elucidate, the different characteristics of the rare elements of tbis group. Never before was it imagined that an industry in rare earths could develope in such a manner and place at the service of Science these tons of rare oxides, such as was shown to be the case by Dr. Otto Witt, on his visit to the Welsbach factory at Gloucester city, New Jersey. This factory treats daily such quantities of monazite sands that M. Witt reports that he actually saw 1000 kilos. of oxide of lanthanum, several tons of salts of cerium, and some hundreds of kilos. of oxide of thorium.

A NEW METHOD OF FRACTIONATION OF THE YTTRIA EARTHS.

By C. URBAIN,

I HAVE studied a large number of the yttria salts from the point of view of their behaviour during fractionation.

The derivatives which have given me the best results by fractional crystallisation are the ethylsulphates. These salts, which form magnificent crystals in the form of hexagonal prisms, have been described by M. Alen and determined by M. Topsoë. They are easily prepared by double decomposition between the yttric sulphates and ethylsulphate of barium.

When fractionated they behave in the following manner:—The first crystals which are formed, though hardly coloured, show a pale orange tint, and are very poor in earths having absorption bands; they also have a lower atomic weight than the mother-liquors.

If the solution contains didymium the didymium accumulates at one end to such a degree that one cannot find it in the other portions of the fractionation, although the ethylsulphate of didymium is very soluble in the absence of the yttria earths. Among the earths of the erbia group found in the first crystals, the element X of Soret is observable with a spectrum decidedly stronger than that of the fresh erbium.

TABLE I.—*Yttria Earths from Æschynite.*

Divisions on the micrometer.	Wave-lengths.	Elements.	First crop of crystals.	Second crop of crystals.
32	654	Erbium.	Faint.	Fairly strong.
34	640	Holmium	Do.	Do.
54—56	582—572	Didymium.	Faint and diffused.	Faint.
67	543	X.	Do.	Do.
69	540	Erbium.	Do.	Do.
72	536	X.	Faint.	Strong.
78	523	Erbium.	Do	Fairly strong, blurred on the right.
79	520	Didymium.	Very faint.	Faint.
100	484	X.	Faint.	Strong.
108	474	Dysprosium.	Very faint.	Faint.
125—130	453—450	Do.	Faint.	Very strong.

This table shows that the fractionation of the yttric ethylsulphates of the monazite sands goes on in a manner very similar to that of æschynite. It further shows that fractionation in alcohol is very similar to that in water with regard to didymium, but that the inverse is the case with the yttric earths having absorption bands; these

TABLE II.—*Yttria Earths from the Monazite Sands.*

Divisions on the micrometer.	Wave-lengths.	Element.	Mother-liquors. Alcoholic solution.	Second crop of crystals.
31	654	Er.	Faint.	Fairly strong.
34	640	X.	Do.	Do.
54—56	582—572	Di.	Very faint.	Faint, blurred.
66	546	Er.	Do.	Faint.
67	543	X.	Do.	Do.
69	540	Er.	Do.	Do.
72	536	X.	Faint.	Strong.
78	523	Er.	Fairly strong.	Fairly strong.
79	520	Di.	Faint.	Faint.
99	484	(X).	Doubtful.	Strong.
101	482	Di.	Do.	Faint.
108	474	Dy.	Do.	Faint.
124—129	453—450	Dy.	Faint.	Strong.

accumulate in the first crops from the alcoholic fractionations.

The spectral study of these portions has been completed by the determination of the atomic weights. By this method of procedure I have confirmed the results found by M. Budischowski and myself (*Comptes Rendus*, 1897) by the fractionation of the acetyl-acetonates, and those obtained by MM. Schutzenberger and O. Boudouard (*Comptes Rendus*, 1897) by the fusion of the nitrates and fractionation of the sulphates. The orange tint of this oxide seems to point to the presence of terbium. Further, the absorption spectrum at this limit, although very faint, shows the presence of at least four substances of high atomic weights.

I should therefore imagine, until the contrary is proved, that this substance is only impure yttrium.

The next crystals deposited in the fractionation of the ethyl-sulphates become more and more pink. The X spectrum of Soret gradually diminishes. The spectrum of dysprosium appears to be more persistent. We next obtain crystals whose solution only gives a very intense spectrum of fresh erbium, and in which the thulium bands seem to be present. The spectrum of the crystals which are finally deposited become gradually fainter, and we finally obtain a mother-liquor which no longer crystallises sensibly and which no longer shows any absorption bands. This earth has a high atomic weight and its oxide is perfectly white.

TABLE III.—*Spectrum of the Last Crystals.*

Micrometer division.	Wave-lengths.	Elements.	
24	684	Tm (Thulium).	Faint.
31	654	Er.	Faint.
69	540	Er.	Very faint.
78	523	Er.	Strong.
99	485	(X).	Strong.
115—120	469—463	Tm ?	Faint.
128	451	Er.	Faint.

In conclusion, we can deduce from the measurements here given that the yttric earths separate in the following order when fractionated as ethylsulphates:—Yttrium, terbium, holmium and dysprosium, erbium, ytterbium.—*Comptes Rendus*, cxxvi., No. 11.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 17th, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

MESSRS. A. J. Buller Cooper, J. Murray Crofts, R. S. Morrell, T. Cunningham Porter, F. F. Renwick, and Harold C. Sayer, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Oscar Julian Steinhart, Ph.D., 4, Palace St. Mansions, S.W.; Samuel A. Tucker, Ph.D., Columbia University, New York; Ernest Witham, The Grammar School, Rotherham.

ANNOUNCEMENT BY THE COUNCIL.

The PRESIDENT announced that notice of the following Resolutions to be proposed at the Annual General Meeting by Messrs. Hartog and Harden had been received:—

Resolution I.

That in order to carry out the suggestion of Mr. Cozens-Hardy, Q.C., communicated by the Council to the Society at the meeting held on February 17th, 1898 (*Proc.*, 1898, xiv., 38), the following steps shall be taken

TABLE IV.—*Intermediate Fractions.*

Micrometer division.	Wave-length.	Elements.	I.	II.	III.	IV.
24	684	Tm.	Faint, sharp.	—	—	—
27·5	675	Er.	Faint, stronger than 684.	Very faint.	Extremely faint.	—
31	654	Er.	Strong.	Strong.	Fairly strong.	Fairly strong.
34	640	X.	Faint, like 684.	Faint.	Do.	Do.
66	546	Er.	Very faint.	Extremely faint.	Doubtful.	—
69	540	Er.	Fairly strong.	Fairly strong.	Faint.	Very faint.
72	536	X.	Fairly strong, sharp, fainter than 540.	Fairly strong, stronger than 540.	Fairly strong, stronger than 640.	Strong, blurred on the right.
78	523	Er.	Very strong, blurred up to division 80.	Very strong, blurred up to division 80.	Very strong, blurred on the left.	Strong, blurred on the left.
97	489	Er.	Faint, wide, blurred on the left.	Faint, wide, blurred on both sides.	Very faint, wide, blurred.	Extremely faint.
99	485	(X).	Strong, sharp, stronger than 654.	Strong, blurred on the right.	Very strong, blurred.	Strong, nebulous.
108	474	Dy.	Very faint.	Very faint.	Very faint.	Very faint.
117	461	Tm ?	Doubtful.	—	—	—
129	451	Dy.	Strong, sharp, blurred on the left.	Very strong, blurred on the left.	Blurred, but the strongest in the spectrum.	Very strong.
136	444	(Di).	Faint, stronger than 489.	Faint, fainter than 489.	Doubtful.	—

to ascertain the wishes of the whole Society with regard to the desirability of obtaining a Supplemental Charter for the purpose of enabling Fellows to record their votes at the Annual Election of the Officers and other Members of the Council by proxy or post.

(1) The following papers shall be printed and distributed to the Fellows of the Society not later than April 14th:—

(*a*) The Chemical Society, Burlington House, Piccadilly, London, W.

Dear Sir,—In accordance with the Resolution passed at the General Meeting of the Chemical Society held on March 31st, 1898, we are instructed to request you to be good enough to—

(i.) Answer the question printed below, by writing "Yes" or "No" in the space marked for the purpose.

(ii.) Fold this paper with the blank side outermost, place it in the envelope "A" provided, close the envelope, and write your signature legibly *outside*.

(iii.) Enclose the envelope "A" in the stamped envelope "B," and return this by post to the Secretaries on or before May 14th next.

We are, faithfully yours,
(Signatures of Secretaries.)

Are you in favour of the proposal that a Supplemental Charter should be applied for to the Privy Council so as to enable Fellows to vote at the Annual Election of the Officers *by post or proxy?*

(Here write "Yes" or "No")."

(*b*) An envelope marked thus:—

The Chemical Society. *Re* Charter. A.

Voting Paper.

Please sign legibly here.....

(*c*) An envelope stamped with a penny stamp, and marked thus:— B.

Re Application for Supplemental Charter.

The Secretaries of the Chemical Society, Burlington House, London, W.

(2) At the next meeting held after May 14th the envelopes shall be opened, and the voting papers placed, without being unfolded, in a balloting-box, and they shall be counted by a sufficient number of scrutators, to be appointed by the presiding officer. The signatures on the envelopes shall be at the same time checked against an official list of Fellows of the Society, and shall be preserved for a year.

Resolution II.

If a majority of the votes recorded in accordance with the method prescribed by the foregoing Resolution be in favour of an application being made for a Supplementary Charter for the purpose named, the Council shall be, and are hereby instructed, without any further proceedings, to make the necessary application without delay.

To this notice of Resolutions the following reply had been sent:—

Chemical Society, Burlington House, W., March 17th, 1898.

Dear Sirs,—The Council have carefully considered the proposed Resolutions which you have forwarded to the Secretaries, notifying them that you intend to move them at the Annual General Meeting.

We are, in the first place, to point out that the effect of passing such Resolutions would be precisely the same as passing a Bye-law to enable Fellows to vote by proxy or through the post on this question, and that Mr. Cozens-Hardy, Q.C., has already advised that any such Bye-law would be repugnant to the Charter.

We are directed to say that this of itself would be sufficient to make the proposed Resolutions out of order, but there are other grounds on which the Council are advised that such Resolutions cannot be submitted to a General Meeting.

The Council are advised that in view of the opinions of Mr. Cozens-Hardy, such Resolutions would not be in order, because they propose to deal with a question which is outside the scope of matters which can be decided at a General Meeting of the Society.

They are also advised that even if such Resolutions were passed they would have no power to act upon them, because in considering whether the Fellows really desire the change proposed, regard must not be had only to those who are present in person at a meeting (and still less to a bare majority of Fellows voting, as you propose), but to the wishes of the whole body of the Fellows. You will remember that Mr. Cozens-Hardy thinks that an application for a Supplemental Charter would probably not be listened to unless it represented the practically unanimous view of the Fellows, and that any active opposition by even a small minority would probably be fatal.

The Council are further advised that it would be *ultra vires* to expend any part of the funds of the Society in giving effect to the proposed Resolutions or in applying for a Supplemental Charter.

In these circumstances, we are directed to inform you that it would be the President's duty to refuse to put such Resolutions to the meeting.

We are also to point out that it would be open to any Fellows of the Society, at their own expense, to send out the circulars referred to in the Resolutions, and that if it should be found that the Fellows were practically unanimous in desiring that application should be made for a Supplemental Charter, this could be applied for by them at the like expense, and that in the event of there being no opposition Her Majesty might be pleased to direct that such expenses should eventually be paid out of the funds of the Society.

We are, dear Sirs,
Your obedient Servants,

John M. Thomson, } *Honorary*
Wyndham R. Dunstan, } *Secretaries.*

Arthur Harden, Esq.
P. J. Hartog, Esq.

Of the following papers those marked * were read:—

*34. "*The Reduction of Bromic Acid and the Law of Mass Action.*" By Winifred Judson, B.Sc., and J. Wallace Walker, M.A., Ph.D.

The authors have investigated the velocity of the reduction of bromic acid by hydrobromic acid, and find that, in the presence of a large quantity of sulphuric acid, the reaction is bimolecular, whereas in the absence of sulphuric acid it is tetramolecular. The results are in agreement with the conclusions drawn by Noyes (*Zeit. Phys. Chem.*, 1896, xix., 599) from the experiments of himself and others on the reduction of bromic acid by hydriodic acid. The explanation put forward is that the stage of the reaction, which requires a measurable time for its completion, is expressed by the equation—

$$\overset{+}{2H} + \overset{-}{Br} + \overset{-}{BrO_3} = HBrO + HBrO_2,$$

and that the bromous and hypobromous acids are instantly decomposed by the hypobromic acid present. A further result obtained is that the reduction of bromic acid by hydriodic acid takes place 58·5 times faster than by hydrobromic acid, and that, therefore, although the latter is produced from bromic by hydriodic acid, its presence in no way vitiates the conclusions drawn by Noyes from that reaction.

*35. "*The Action of Ferric Chloride on the Ethereal Salts of Ketone Acids.*" By R. S. Morrell, M.A., Ph.D., and J. M. Crofts, B.A., B.Sc.

When anhydrous ferric chloride dissolved in absolute ether is added to an ethereal solution of ethylic ketophenylparaconate, a red oil separates. This, when washed with absolute ether, becomes solid, and is, most probably, represented by the formula $FeCl_2(C_{13}H_{11}O_5)$. Water decomposes the compound with formation of

the basic ferric salt of ethylic ketophenylparaconate, $Fe(OH)(C_{13}H_{11}O_5)_2$, and ferric chloride.

The ethylic salt of the lactone of oxalcitric acid yields with ferric chloride in absolute ether solution a red oil, which does not solidify, and is most probably an addition product, represented by the formula $FeCl_3,C_{14}H_{18}O_9$. It loses hydrochloric acid slowly in a vacuum. On treatment with water, it yields the ferric salt of the lactone of ethylic oxalcitrate, $Fe(C_{14}H_{17}O_9)_3$, and ferric chloride.

In the case of ethylic acetoacetate and ethylic benzaldiacetoacetate, purple oils are obtained by the action of anhydrous ferric chloride. The purple substances have not as yet been prepared in a sufficiently pure state to justify the authors in assigning formulæ to them.

*36. "*Note on the Volatility of Sulphur.*" By T. C. PORTER, M.A., &c.

During the analysis of some pumice rock from Tenerife, the author was led to the conclusion that sulphur is volatile at 100°. Several glass tubes were carefully cleaned, into which specimens of sulphur of varying physical condition and purity were placed. Some of the tubes were exposed to the air, others were exhausted. After being exposed to a temperature of 100° for some minutes, it was observed that, as was to be expected, the better the vacuum the more rapid is the sublimation of the sulphur. The sublimate consists at first of very pale yellow drops, which possess little viscosity, and remain unchanged in some cases even at 10° for days. Rhombic octahedra and prismatic sulphur are occasionally formed together; the former crystals sometimes grow at the expense of the drops. Sulphur does not yield a perceptible sublimate at ordinary temperatures, in a "good vacuum," even after a year. The two forms S_α and S_β therefore have their transition point between 90° and 100°.

DISCUSSION.

Professor MCLEOD said that about 1870 Mr. Douglas Herman had experimented on the volatility of various substances in vacuous tubes, although he believed the results have never been published. Mr. Herman found that sulphur could be volatilised in a vacuum when heated to the temperature of boiling water, and that the vapour condensed in drops on the cool parts of the tube, and remained liquid for many days. Octahedral crystals were formed at the expense of the drops in the neighbourhood of the crystals, the drops gradually evaporating whilst the crystals increased in size; prismatic crystals were very rarely seen. When phosphorus is heated *in vacuo* by the warmth of the hand, its vapour also is deposited in drops, although, as in the case of sulphur, the vapour had not been heated to the melting-point of the solid. Iodine at once forms crystals under similar conditions, no liquid being deposited.

The PRESIDENT said that, in a lecture on liquid atmospheric air, in 1893 (*Proc. Roy. Inst.*, xiv., 7), he had described the use of sulphur in the construction of vacuum vessels for the storage of liquid air, and had shown that in such vacua cooling with liquid air or oxygen was sufficient to produce a visible distillation of sulphur at ordinary temperatures. The vapour tension of sulphur at 100° amounts to 0·06 m.m., so that the tension is comparatively high in Mr. Porter's experiments, considering that mercury distils rapidly under a pressure of one-millionth of an atmosphere, as shown by the application of liquid air. He also remarked that phosphorus distils practically instantaneously.

*37. "*Cannabinol.*" By T. B. WOOD, M.A.; W. T. N. SPIVEY, M.A.; and T. H. EASTERFIELD, M.A., Ph.D.

The authors have continued their examination of cannabinol, the toxic resident constituent of Indian hemp (*Trans.*, 1896, lxix., 539). The substance boils with slight decomposition at about 400°, its absorption spectrum shows no characteristic bands, its vapour-density at the temperature of boiling sulphur corresponds with the formula $C_{18}H_{24}O_2$, already assigned to the compound.

An account is given of the reaction of cannabinol with acetic anhydride, benzoyl chloride, and phosphoric anhydride; the results indicate that one hydroxyl group is present. In the case of acetic anhydride or acetyl chloride, however, a crystalline compound melting at 75° is one of the products of the reaction. The authors assign the formula $C_{15}H_{18}O_2$ to this compound. The same compound has recently been described by Dunstan and Henry (*Proc.*, 1898, xiv., 44, Feb. 17), who ascribe the formula $C_{18}H_{23}OAc$ to it. Fuming hydriodic acid gives no methyl or ethyl iodide when boiled with cannabinol. Reduction with hydriodic acid in sealed tubes produces a hydrocarbon, $C_{10}H_{20}$.

By long-continued boiling, with or without dehydrating agents, a hydrocarbon, $C_{10}H_{16}$, is formed.

Oxidation with aqueous chromic acid, alkaline, or acid permanganate, or dilute nitric acid, is accompanied by the production of a caproic acid, lower fatty acids being probably produced at the same time. The action of fuming nitric acid upon cannabinol dissolved in cold glacial acetic acid removes one carbon atom as carbonic anhydride, and produces a red, amorphous substance, which gives numbers on analysis agreeing with the formula $C_{17}H_{20}N_2O_6$. This substance, when boiled with nitric acid, yields a light red substance, $C_{17}H_{20}N_2O_8$, which upon further oxidation yields, amongst other substances, a yellow acid crystalline compound, $C_{13}H_{15}N_2O_5$, which forms sparingly soluble crystalline sodium, ammonium, and silver salts, and is probably a dinitrophenol, and a compound, $C_{11}H_{11}NO_4$, the properties of which agree closely with those of the "oxycannabin" of Bolas and Francis (CHEM. NEWS, 1871, xxiv., 77). This compound has the properties of a nitro-lactone, as has been already shown by Dunstan and Henry (*Proc., loc. cit.*). Corresponding crystalline potassium and silver salts have been prepared and analysed. The name cannabinic acid is proposed for the unnitrated parent oxy-acid.

Amido-cannabinolactone, $C_{11}H_{11}O_2NH_2$, is obtained in colourless crystals melting at 119°, when the nitro-lactone is reduced either by hydriodic acid or by tin and hydrochloric acid. The base is readily re-crystallised from hot water; its salts cannot be re-crystallised from water without decomposition.; the hydriodide and platinochloride have been analysed.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 25th, 1898.

Mr. SHELFORD BIDWELL, President, in the Chair.

Mr. A. A. CAMPBELL SWINTON read a paper and showed experiments upon "*The Circulation of Gaseous Matter in a Crookes Tube.*"

The stream-lines within a Crookes tube are investigated by observing the direction and speed of rotation of a mica radiometer-mill, mounted on a sliding rod, so that it can be moved along a line at right-angles to the line joining the electrodes. The axis of the mill is at right-angles to both these lines. If the mill is adjusted to a position between the flat-plate and the cup electrodes, with its axis just sufficiently low to prevent equal and opposite simultaneous action on the top and bottom vanes, it rotates always in the direction indicating a stream from cathode to anode; the speed is greater when the flat plate is the cathode. If, however, the mill is now moved below this line, a point is reached at which rotation ceases, and below this neutral point the rotation is suddenly reversed. Reversal is only to be observed with high degrees of exhaustion; the rotation is never so rapid as in the first position. The mill rotates and the reversal may be observed whether cup or plate is made cathode, and the direction of rotation below the neutral point is always opposite to that in the position above it. A small

Wimshurst machine is as effective as an induction coil in producing these effects.

The experiments are intended to establish the existence, at high degrees of exhaustion, of a true anode-stream, *i.e.*, a stream that travels from anode to cathode just in the same manner as the cathode stream flows from cathode to anode. This anode-stream is charged positively; it is exterior to the cathode-stream; its velocity is less than that of the cathode-stream, but its velocity increases as the vacuum is improved. It seems probable that, in high vacua, some portion of the positive electricity passing through the tube is carried by the positively charged atoms or particles that constitute the anode-stream. At lower degrees of exhaustion, the discharge passes through the tube chiefly by interchange of charges from molecule to molecule—a Grothüs chain. At very high vacua, however, when the mean free path is considerable, there may be to some extent a regular and complete circulation of positive and negative atoms, some of which pass from anode to cathode and *vice versâ*, and deliver up their charges, not by interchange, but by direct convection, to the electrodes of opposite sign.

Prof. Boys said he did not feel altogether convinced by the experiments that the rotation of the mill was due to simple mechanical motion of the particles of matter between the electrodes. The weight of air left in the tube at such high degrees of exhaustion was extremely small; it was difficult to realise that its impact could produce the sudden mechanical effect observed at the moment of the reversal of the rotation of the mill.

Mr. Wimshurst thought it important to keep in mind the existence of mercury vapour in the tube. He also referred to some experiments in which a bar of metal was used to explore a focus tube, by observations of the changes of luminosity produced in different positions.

Dr. Chree said that if the rotations of the mill could be shown to indicate a velocity of the particles, of the same order as that observed in Crookes's experiments, it was safe to assume the existence of a similar cause. This might be important in deciding as to the general truth of the bombardment theory of Crookes. He asked whether the rotation had been investigated within the dark space around the cathode.

Mr. Appleyard suggested that in tracing the cause of the rotation, it would lead to simpler results if the vanes of the mill were made of some light conducting substance. Mica introduced difficulties, owing to its retention of the charges.

Prof. Boys pointed out that this could be done by gilding the mica.

Mr. Campbell Swinton, in reply, said that the objection raised by Prof. Boys to the mechanical theory of the rotation would apply equally to the whole theory of electro-radiometry, including the case of the mill used originally by Crookes in the direct path of the cathode stream. But it must be remembered that, although the mass of matter present within the tube was very small, its velocity was proportionally great; it was of the order of 9000 kilometres per second. Hence, the contained matter might be conceived as capable of producing the observed acceleration, and Crookes's bombardment theory might safely be adopted as a good working hypothesis. In the tubes used for these experiments, the exhaustion was carried so high that the negative dark space appeared to fill the whole tube. He had, so far, only tried mica for the vanes, but he thought it would be important to observe the results with a substance that did not retain the charges.

Mr. A. Stansfield then read a paper on "*Thermo-electric Pyrometers*."

In obtaining photographic records of the readings of thermo-electric pyrometers, the range of measurement is limited by the size of the photographic plate. For long ranges of temperature, the sensitiveness of the galvanometer must therefore be small.

When it is desired to examine the temperature changes in detail—as, for instance, at the melting-points and freezing-points of metals—it is necessary to employ some device for giving a more open scale for the short temperature ranges that include those particular points. For this purpose two galvanometers are arranged in parallel, and so that they have their deflections recorded on the same photographic plate. The less sensitive galvanometer covers the entire range of temperature throughout an observation; the other is brought into use for magnifying special portions of the range. In this latter case part of the electromotive force of the thermo-couple is compensated by an opposing electromotive force, applied at two points of the circuit, from a battery of Clark cells in series with a high resistance.

The recording apparatus consists of a photographic plate mounted on a float that rises steadily when water is admitted into a cylinder. The source of light is a glow-lamp, enclosed in a wooden box. A brass tube with a rectangular diaphragm at the end nearest the lamp cuts off all light, except that from a selected piece of vertical filament. Light from this filament is reflected by the plane galvanometer-mirror, and is focussed upon the photographic plate by a lens in front of the galvanometer: this method was suggested by Prof. Boys. The "cold" junctions of the thermo-couple are both inserted into a hypsometer. Very serious discrepancies exist between the indications of couples having nominally the same composition; they are too great to be attributed to accidental differences in the constitution of the alloys. Although with platinum alloys, coupled with platinum, 10 per cent of iridium gives a more powerful couple than 10 per cent of pure rhodium; the partial substitution of iridium for rhodium very considerably lowers its thermo-electric power. This result suggests that the change in the thermo-electric power of a metal depends upon the extent to which it is saturated with the alloying metal; thus 10 per cent either of rhodium or iridium would more completely saturate the platinum than would 10 per cent of a mixture of the two metals. The author discusses a series of curves derived from his experiments. He concludes that, thermo-electrically, there may be two classes of metals:—(1). The ordinary metals, for which the curve representing the first differential of electromotive force with respect to temperature is a straight line; and (2). The platinum metals, together with a few such as nickel and cobalt, for which the curve of this differential muliplied by the absolute temperature is a straight line.

Dr. Chree discussed the curves, and asked how far stirring affected the results; he was inclined to think that stirring was a mistake.

Mr. A. Campbell enquired whether the galvanometer kept its zero sufficiently well throughout the tests.

Mr. Stansfield, in reply, said he had also come to the conclusion that stirring was a mistake; it was a mistake to use a large quantity of metal. The pyrometers were sensitive to about a tenth of a centigrade degree. He had experienced great difficulty with regard to the zero of the galvanometer.

The President proposed votes of thanks to the authors, and the meeting adjourned until April 22nd.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. 1898, No. 1.

The New Development of the Lighting Effect of Flames.—H. Bunte.—Contains a history of the gas industry, the introduction of glow lamps, and the discovery of acetylene from calcium carbide.

The Products of the Explosive Decomposition of Nitro-Compounds. — Christian Göttig. — The author points out that the numbers given for the composition of the gases formed by the explosion of gun-cotton by different investigators were very variable. He therefore makes a careful investigation of the solid and gaseous products formed by the explosion of gun-cotton having the composition, barium nitrate 9·83 per cent, nitro-toluol 22·22 per cent, and nitro-cellulose 67·96 per cent. The solid products consist of carbon 9·51 per cent, barium carbonate 64·44 per cent, and a residue insoluble in acid 26·05 per cent. The gaseous products consist of oxides of nitrogen 10·75 per cent, carbon dioxide 27·48 per cent, carbon monoxide 36·02 per cent, methane 9·01 per cent, hydrogen 1·94 per cent, and nitrogen 14·8 per cent.

The Action of Benzhydrazide on Glucose. — Georg Pinkus.—The author finds that in alkaline solution glucose is decomposed, in presence of benzylhydrazide, into glyoxal and methylglyoxal, which are removed from further action by reason of the insolubility of the osazone formed. He suggests that the methylglyoxal is an intermediate product in the long-known formation of lactic acid from sugar in alkaline solution.

Constituents of Beech-Tar.—C. Harries.—Alterberg has isolated from the volatile parts of the tar oil of *Pinus sylvestris* a body for which he found the formula C_5H_6O. He recognised this as methylfurane, and gave to it the name Sylvan. The author has now found that this body can also be obtained as an ingredient of beech-tar creosote (the part boiling between 60° and 70°). To get rid of aldehyd and ketone from this substance it is treated with sodium bisulphite, the remainder shaken up with NaOH solution, and then dried with K_2CO_3; it is then fractionated. The sylvan boils at 65° under 759 m.m. pressure, and has sp. gr. 0·827 at 18°. It is a light, mobile, colourless liquid, of ethereal smell, which, after standing for twenty-four hours, becomes bright yellow. This colour can be removed by treating it with a very small quantity of alcoholic HCl.

Some Syntheses with Chlorfumaric Ester.—Walter Beckh.—The condensation of ethenyltricarboxylic ester and chlorfumaric ester by means of sodium methylate gave, as chief product, a butylene pentacarboxylic ester. The free acid was only obtained in a very impure condition. By further action of sodium methylate, a molecule of alcohol split off and a substance was obtained to which the author assigns the name tetrylone-tetracarboxylic ester. Amylene pentacarboxylic ester was prepared in a similar way by condensation of chlorfumaric ester with sodium carboxyglutaric ester, and when treated with sodium ethylate it also lost a molecule of alcohol, yielding a reduced benzene compound.

Nitrogen-free Decomposition Products of Morphine.—E. Vongerichten.—The author finds that phenanthrene derivatives can be obtained from morphine derivatives, not only on distillation with zinc dust, but also with chromic and acetic acids. He obtains a phenanthrene quinone derivative. Acetylmethyl morphol from methylmorphmethane gives a very good yield of acetylmethylmorphol quinone, which shows that morphine bears a very close relation to phenanthrene.

Methylating of Hydrazin Hydrates.—C. Harries and T. Haga.—(*a*) Action of Methyl Iodide on Hydrazin Hydrate in the presence of KOH.—If hydrazin hydrate is shaken up with methyl iodide, in the cold, hydriodide of hydrazin is formed, which can be decomposed by KOH, and again treated with methyl iodide. The reaction may be represented by the following equations :—

$$2NH_2.NH_2+I.CH_3=IH.NH_2.NH_2+NH_2.NH.CH_3.$$

$$2CH_3.NH.NH_2+I.CH_3=IH.NH_2.NH.CH_3+NH_2N(CH_3)_2.$$

$$(CH_3)_2N.NH_2+ICH_3=I(CH_3)_3.N.NH_2.$$

Trimethylazonium iodide is somewhat soluble in alcohol and amyl alcohol on boiling; it crystallises in the same way as NH_4Cl, and decomposes before melting at about 235°. (*b*) Action of Methyl Iodide on Hydrazin Hydrate without KOH.—With excess of hydrazin hydrate, methyl hydrazin and dimethyl hydrazin are formed, but no azonium salt or a very little. When, on the contrary, excess of methyl iodide is used, besides hydrazin hydriodide, trimethylazonium iodide is obtained.

A Method of Gravimetrically and Gasometrically estimating Hydroxylamine and Hydrazine.—K. A. Hofmann and F. Küspert.—The authors estimate hydrazin as well as hydroxylamine, through oxidation with dilute vanadic solution containing H_2SO_4. The evolved N is collected, and the partially reduced solution is titrated back to vanadic sulphate, by means of permanganate. The reaction may be represented by the equations :—

$$(i.)\ 2NH_3O + O = N_2 + 3H_2O$$

$$(ii.)\ N_2H_4 + 2O = N_2 + 2H_2O.$$

On warming the solution to about 60° the N comes off quantitatively, and can be measured. The contents of the flask are titrated with permanganate solution, and this result can be used to check the volumetric measurement of the nitrogen.

Nitration of Carbohydrates.—W. Will and F. Lerze.—The authors have made experiments on the nitration of the whole class of sugars, and have succeeded in obtaining pure and in many cases crystalline products. From glucose and xylose they were unable to obtain crystalline products. Generally the best results were obtained when HNO_3 at 0° (sp. gr. 1·52) was added to the finely-powdered substance until it was dissolved, and cold concentrated H_2SO_4 (sp. gr. 1·84) dropped slowly on to the solution. The following products were obtained:—(1) Tetranitrates of the pentoses; (2) of the hexoses, crystalline pentanitrates of glucose, galactose, and mannose, and a trinitrate of lævulose; (3) hexanitrates of heptose. Among the disaccharides, cane-sugar, milk-sugar, and maltose are found to give octonitrates as higher products of nitration.

Chemiker Zeitung.
1898, No. 11.

Formation of Perchlorates of the Alkalies and Alkaline Earths by Electrolysis.—F. Winteler.—By using platinum or peroxide electrodes, aqueous solutions of the chlorides of the alkalies and alkaline earths can be electrolysed, hypochlorites and chlorates being formed. Under certain circumstances the perchlorates can be formed also. References are found in the literature on the subject to the turning of $KClO_3$ into $KClO_4$ between platinum electrodes; but it is remarkable that none of the patents for the preparation of chlorate by electrolysis take this into consideration, and in the new books it is passed over completely. When the electrolysis has proceeded so far that only chlorate is found in the solution, this chlorate will oxidise further between platinum or peroxide electrodes under the following conditions:—(1) When there is an acid solution round the anode. (2) When the anode is at a low temperature. (3) When there is a current density of 4—12 ampères. (4) When the concentration of the electrolyte is as great as possible. Suppose, for example, at ordinary temperature, a saturated neutral solution of $KClO_3$ is electrolysed without using a diaphragm, the electrodes being kept at 10°, 75 per cent of the oxygen which ought to separate out is used to convert the chlorate to perchlorate. A saturated $NaClO_3$ solution (1 : 1), under exactly similar circumstances, is transformed into perchlorate with a yield of 95 per cent. When nearly the whole of the chlorate is transformed, the yield begins to decline very rapidly. The direct cooling of the electrode is of great importance. The apparatus in which the electrolysis takes place must be so arranged that the electrode comes in contact with

the electrolyte on one side only, otherwise the current density cannot be indicated accurately, for only the side turned to the cathode comes into consideration. The cathode density is immaterial, and depends only on the voltage. Other things being equal, the yield is the greatest when the anode current density is 8—12 ampères. Greater or less density diminishes it. Even a chlorate solution, to which 4 per cent of alkali has been added, changes into the required perchlorate. The stirring up of the anode and cathode solutions is not done mechanically, but by means of the evolved gas. An intense smell of ozone is characteristic of the formation of perchlorate. Ozone is evolved in such quantities from a concentrated chlorate and perchlorate solution that rubber tubing and connections will be destroyed in a few minutes, and it would be worth while to use this electro-chemical method for preparing ozone. If carbon is used for the electrodes it is very quickly destroyed, no formation of perchlorate taking place. The use of any other metal than platinum or iridium is out of the question, since the anode takes away ClO_3 and forms a soluble salt with it. An interesting observation, which has been lost sight of recently, is that of A. Riche, by which dilute HCl is turned into $HClO_4$ by electrolysis between platinum electrodes. According to my experiments, the conditions favourable for this are identical with those of the formation of the perchlorate. The perchloric acid will be more concentrated the lower is the temperature of the electrolyte—the best of all being a temperature at which no gaseous chlorine can escape.

MISCELLANEOUS.

The Chemical Laboratory at Wiesbaden.—The hundredth term at the Chemical Laboratory Fresenius will shortly begin. The Laboratory was established on the first day of May, 1848, and the celebration of the fifty years of its existence will shortly take place. Its founder, Geh. Hofrath Professor R. Fresenius, died on June 11th last, and since his death the Laboratory has been carried on by his sons, Professor Dr. Heinrich Fresenius and Dr. Wilhelm Fresenius, and his son-in-law, Dr. Ernst Hintz, in co-partnership; they will continue the institution in the same manner as before. The list of the enrolled students of the Winter Session 1897-98, just published, shows an equal attendance at the Laboratory as in former years. There were fifty-three students on the books during the Winter Term 1897-98. Of these, forty were from Germany, four from England, two from Austria, two from Luxemburg, one from France, one from Spain, one from Sweden, one from Russia, and one from Brazil. Of the students, forty-four were working exclusively in the chemical laboratory, seven exclusively in the bacteriological department, and one both in the chemical and bacteriological branches of the Institute. There were employed three assistant teachers in the instructing laboratories, and twenty-five assistants in the different departments of the Laboratory (Versuchsstationen). Besides the Directors (Professor Dr. H. Fresenius, Dr. W. Fresenius, and Dr. E. Hintz), Messrs. G. Frank, M.D., W. Lenz, Ph.D., L. Grünhut, Ph.D., and architect J. Brahm, belong to the faculty of the College. The next Summer Term begins on April 25th. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory on behalf of manufacture, trade, mining, agriculture, and hygiene.

The Titration of Stannous Salts with Iodine.—S. W. Young.—The author states that the reaction between stannous chloride and iodine, by which the former is oxidised, takes place smoothly in acid solution, and may be utilised for the determination of tin. The iodine solution is standardised against potassium bichromate with the intervention of a stannous chloride solution of known value. The statements are made that "thiosulphate cannot be satisfactorily used in acid solution to titrate against iodine," and that "the standard of iodine by thiosulphate is likely to be a trifle high;" but no authorities are quoted nor experimental data offered in support of these assertions.—*Journ. Amer. Chem. Soc.*, xix., 809.

The Analysis of Raw Sulphide of Sodium.—F. Jean. — The crystals of raw sulphide of sodium are crushed, and 10 grms. dissolved in water and diluted to 1 litre. To 10 c.c. of this solution starch is added; it is then titrated with decinormal iodine. To another 10 c.c. of the original solution a quantity of sulphate of ammonium (at 6·7 grms. per litre) is added, in quantity equal to the number of c.c. of the solution of iodine used in the first case; then add about 30 c.c. of water and distil over the ammonia set free by the monosulphide of sodium. Then boil to drive off the sulphuretted hydrogen, and titrate the excess of acid: 1 c. c. of decinormal acid saturated with ammonia corresponds to 0·0039 grm. of monosulphide of sodium. The liquid remaining in the retort is titrated with a N/10 solution of iodine: 1 c.c. of the iodine corresponds to 0·0079 grm. of hyposulphite of soda.—*Journ. de Pharm. et de Chim.*, vii., No. 4.

The Solubility of Theobromine in Aqueous Solutions of Salts of an Alkaline Reaction. — M. Brissemoret. — At a temperature of +15° a solution of 14·80 grms. of trisodic phosphate in 80 c.c. of water will dissolve 3·50 grms. of theobromine. One would at first be inclined to think that a combination took place between the trisodic phosphate and the theobromine, as these weights agree with their molecular weights. As a matter of fact, this phenomenon is simply the solution of the theobromine in the alkali set at liberty by the dissociation that the phosphate of soda undergoes on contact with water.—*Journ. de Pharm. et de Chim.*, vii., No. 4.

MEETINGS FOR THE WEEK.

Monday, 4th.—Society of Chemical Industry, 8. "The Bacterial Treatment of Sewage containing Manufacturing Refuse," by W. J. Dibdin, F.I.C., F.C.S.

Tuesday, 5th.—Society of Arts, 8. "The British Empire—its Resources and its Future," by John Lowles, M.P.

CHEMICAL LABORATORY,
WIESBADEN, GERMANY.

DIRECTORS.

Practical Instruction in the Laboratory .. .. Prof. H. FRESENIUS, Ph.D., W. FRESENIUS, Ph.D., E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic)	Prof. H. FRESENIUS, Ph.D.
Experimental Physics	W. FRESENIUS, Ph.D.
Stöchiometry	
Organic Chemistry	L. GRÜNHUT, Ph.D.
Chemical Technology	
Microscopy, with exercises in Microscopic work	W. LENZ, Ph.D.
Chemistry and Analysis of Foods ..	Prof. H. FRESENIUS, Ph.D., W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene	Dr. med. G. FRANK.
Practical exercises in Bacteriology ..	
Technical Drawing, with exercises ..	J. BRAHM.

The next Session commences on the 25th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. Kreidel's Verlag, at Wiesbaden, or to noe of the Directors.

CHEMICAL AND ALLIED TRADES EXHIBITION AND MARKET, 1898.

An Exhibition of the Chemical and Allied Trades will be held at the Agricultural Hall, London, N., from the 13th to the 17th June, 1898, at the same time as the 4th Annual Chemists' Exhibition, and under the same management.

The Chemists' Exhibition is one of the most successful of the trade exhibitions held yearly in London, and is visited annually by a very extensive trade assembly, which includes large numbers of Manufacturing Pharmacists, Wholesale Druggists, Analytical Chemists, Makers of Proprietary Articles, Exporters of Drugs and Chemicals, and numerous Foreign and Colonial buyers.

By taking advantage of this opportunity, the presence of a considerable number of extensive purchasers and consumers of products connected with the Chemical and Allied Trades is assured, and as the Exhibition is being extensively advertised to all interested in these trades throughout the United Kingdom and the Continent of Europe, a very large attendance of those with whom supplying houses desire to do business can be confidently anticipated. Exhibitors will thus have an opportunity to submit their specialities to the inspection of very large numbers of trade buyers, under the conditions most favourable to business, and in circumstances of advantage such as are not afforded to them in this country on any other occasion.

Plans and further particulars can be obtained from Mr. J. F. CANTWELL, Managing Director of the Chemists' Exhibition, 44, Bishopsgate Street Without, London, E.C. Personal enquiries can be made between 11 and 1 o'clock any day except Saturday.

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WORK CARRIED ON AT HOME AND ABROAD.

Estimates given and Plans submitted for the Erection of New Plant and Repairs and Improvement of Old.

RUNCORN, CHESHIRE.

Mr. J. G. LORRAIN, M.I.E.E., M.I.M.E, M.S.C.I.,
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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2002.

ON THE COMPOSITION OF THE ATLANTIC OCEAN.

By C. J. S. MAKIN, F.I.C., F.C.S.

During a recent voyage from the Cape samples were drawn daily about noon in the neighbourhood of the ship's position. These individual samples and their solid contents per 1000 grms. are tabulated below. The whole series (excluding No. 11) were averaged, and the resulting mixture subjected to an exhaustive examination. The analyses were, as far as the writer found practicable, conducted on the same lines as those of the *Challenger* by Professor Dittmar.* Determinations of ammonia and organic matter have also been made: owing to the samples of the *Challenger* waters running short, these estimations were not made on that occasion.

The specific gravity of the average sample was found to be 1·0275 at 15·5°.

Chlorine and Total Solids.

The halogen contents were determined by ordinary volumetric means. The volume (25 c.c.) for determination was delivered from a calibrated burette. The same volume and burette were employed for all the other determinations, excepting bromine and carbonic acid. Gravimetric means were also tried, but abandoned as probably falling short of the truth.

By volumetric means were obtained—

20·729
20·722
20·721

Mean, 20·724 halogens per litre.

By gravimetric means were obtained—

20·713
20·719

Mean, 20·716

20·7240 was finally adopted. Subsequent bromine determinations gave 67·10 m.grms. Hence, deducting the latter figure, 20·6569 grms. chlorine per litre are obtained.

The individual samples were titrated under the same conditions. Professor Dittmar found it quite impossible to arrive at a true estimate of the total solids by the ordinary method of evaporation and drying. Ultimately, the factor 1·8058 was adopted, as it was proved that, by multiplying the total chlorine by it, a figure was obtained giving the total solids with an error of $\pm$ 0·002 per kilo. This factor has been adopted in the tabulated results and the figures thereby obtained reduced to the proportion per 1000 grms.

A study of the relation of the chlorine to the specific gravity resulted in a series of tables from which the average chlorine may be deduced from any given gravity. With the found gravity (1·0275), a total of 20·720 chlorine results. It is not made quite clear in the text if this applies to the total chlorine as such, or the total *halogen* contents. If the latter, then the principle seems to be true, as there only exists a difference of 4 m.grms. per litre in what has been found and the above figure 20·720.

The mean of a number of chlorine determinations in the North and South Atlantic, respectively, give 20·2703 and 19·806 grms. Cl per litre from the *Challenger* samples. These numbers yield total solids 36·604 grms. and 35·765 grms. per litre. Therefore it would seem that the larger number of samples in the present case over the area yields a rather higher rate of total solids. The above figures were obtained from surface water, as were those of the present inquiry. An inspection of the tabulated results shows that there is an excess of chlorine—and, indirectly, of the total solids—in the North Atlantic. This result agrees with the *Challenger* figures above.

Solid Contents of the Ocean at approximately the Determined Locality.

Number of sample.	Latitude.	Longitude.	Contents per 1000 grms.	Remarks.
1	34·02 S	16·00 E	35·89	
2	27·15 S	11·09 E	35·63	
3	23·29 S	7·41 E	35·97	
4	19·42 S	4·16 E	36·19	
5	15·44 S	1·03 E	36·44	
6	11·43 S	2·05 W	36·15	
7	7·48 S	4·58 W	35·84	
8	3·53 S	7·50 W	35·59	
9	0·08 N	10·33 W	35·69	The Equator.
10	4·15 N	13·17 W	35·91	
11	8·15 N	15·42 W	34·51	During a continued heavy rain.
12	12·09 N	17·28 W	35·94	
13	16·26 N	17·49 W	35·83	
14	20·20 N	17·30 W	36·82	
15	24·22 N	16·55 W	36·69	
16	28·28 N	16·15 W	37·39	At Teneriffe; 200 yards from shore, in about 11 fathoms.
17	31·20 N	16·15 W	36·94	
18	34·48 N	15·34 W	36·85	
19	39·08 N	14·10 W	36·47	
20	43·11 N	12·50 W	36·39	
21	46·56 N	10·09 W	36·28	
22	English Channel		35·94	

The average sample yielded 36·31 total solids per 1000 grms. by multiplying the chlorine by 1·8058.

Carbon Dioxide.

Determinations of the alkalinity yield the proportion of CO_2 in the quantity tested. 250 c.c. of sea-water were boiled with an excess of N/10 HCl to a point short of dryness, and the volume restored with boiled CO_2-free distilled water. The excess of acid was titrated back with a corresponding solution of N/10 Na_2CO_3, the titre of which had been determined. By this method the *Challenger* samples yielded from 52 to 62·83 m.grms. CO_2 per litre. Estimations *on the Challenger*, made by Mr. Buchanan, gave 40 to 82 m.grms.

250 c.c. of the present sample were treated in a similar manner; this consequently yields the total CO_2. A second 250 c.c. was boiled down to free it from dissolved CO_2, made up with distilled water, acid added, and boiled down a second time. On making up the volume again with water, and titrating the excess acid in a similar manner, the small proportion of free dissolved CO_2 is calculated. These estimations were performed in duplicate, and gave—

Total CO_2 per litre in m.grms. . ..	63·57
Free ,, ,, ,, . ..	5·11
Combined CO_2 per litre	58·46

Sulphuric Acid.

The determination of this acid does not present any particular source of possible error. It was estimated in the usual manner as $BaSO_4$. The results were—

* "Report of Scientific Results of the Exploring Voyage of H.M.S. *Challenger*." London, 1884.

2·4681
2·4677

Mean, 2·4679 per 100 c.c.

Bromine.

The determination of this halogen was not conducted in the same manner as the *Challenger* samples were treated. Preference, for simplicity, was given to Fresenius's method. Finally, 100 c c. were evaporated to dryness with a slight excess of pure solid sodic carbonate. The residue was extracted, after pulverisation, with four successive portions of absolute alcohol (boiling). The alcohol, after the addition of two drops of soda, was distilled off to dryness, the residue taken up with water and moderate excess of dilute nitric acid, filtered, and the solution precipitated with nitrate of silver. By this procedure, all the alkaline bromide is extracted, and only a small proportion of the chloride. The precipitate was dried and weighed, and the bulk of it removed to a hard glass bulb and chlorinated. From the loss in weight the bromide of silver is calculated and from it the bromine. The results of three estimations gave 67·10 m.grms. per litre; this is, by a singular coincidence, almost in absolute accord with the *Challenger* "surface" water figure of 67·04 per *kilogrm.* Hence the present estimations appear slightly lower per kilo.

Lime.

CaO was estimated in 25 c.c. by volume in the usual manner, and as hereafter mentioned. In the first case, the base was precipitated as oxalate in the cold and allowed to remain overnight. The precipitate was washed by decantation, dissolved in dilute acid, and re-precipitated with ammonium oxalate and ammonia. It was finally weighed as CaO. In the second case, the volume to be examined was saturated with pure oxalic acid in slight excess and boiled. While hot, excess of strong ammonia (0·88) was added, and the mixture boiled for five minutes or until the precipitate became granular. This precipitate also was washed and re-precipitated, and finally weighed as CaO. All the lime estimations were multiplied by the factor 0·91 in the *Challenger* results as a correction for impurity. If this be applied to the present results, the percentage falls manifestly too low—therefore it has not been employed. The figures finally taken were—

0·06514
0·06520

Mean, 0·06518 CaO per cent (volume).

Magnesia.

MgO was determined in the filtrates from the two methods of lime estimation as pyrophosphate with a careful observation and exercise of all details to ensure its complete precipitation. By dissolving the weighed precipitates of pyrophosphate and searching for lime, no evidence of it could be found. The results are rather high when compared with the mean of the *Challenger* figures. If the amounts of CaO and SO_3 be relatively correct, it would almost appear as if the results were even below the truth. This is because the combined total $CaSO_4$ and $MgSO_4$ exceed rather more than is usual the total amount of the $MgCl_2$. The results were of MgO per 1000 c.c.—

2·4269
2·4273
2·4274
2·4267

Mean, 2·4270

Soda.

The *Challenger* procedure was adopted. A measured quantity of the sample was evaporated to dryness with dilute sulphuric acid and ignited, to obtain a residue of normal sulphates. A specially constructed platinum vessel was employed for this in the *Challenger* estimations. The results nevertheless with an ordinary platinum crucible and lid gave constant residues. From the combined sulphates the found quantities of CaO, MgO, and K_2O expressed as sulphates were deducted. The remainder is normal Na_2SO_4, and is calculated into Na_2O or NaCl as desired. The found quantity of Na_2O is corrected by × 1·0043, a factor used in the *Challenger* estimations, and from the corrected value the sodic chloride is determined. The results per litre were—

4·4571
4·4574
4·4587

Mean, 4·4577

Subtracting the found oxides as sulphates:—

CaO 0·06518 to $CaSO_4$	=	0·1583
MgO 0·24270 to $MgSO_4$	=	0·7281
K_2O 0·049952 to K_2SO_4	=	0·0924
		0·9788

4·4577
0·9788

3·4789 Na_2SO_4

This obtained amount converted into the oxide and corrected gives 1·5266 Na_2O, and this is equivalent to 2·8971 NaCl per litre.

(To be continued).

NOTE ON THE

VOLUMETRIC ESTIMATION OF CHROMIUM.

By RUDOLF L. LEFFLER, F.C.S.

A BROTHER chemist, estimating chromium according to Galbraith, expressed as his experience that he could, without transgressing the instructions, find that element in any class of steel or iron.

This peculiarity had been noticed in this laboratory fully eight years ago, and as the method seems to be still largely used and its reliability is open to question, I thought a short extract from a paper read by myself before the Sheffield Society of Engineers and Metallurgists, in March, 1895, might be of interest.

The original instructions consist in dissolving in dilute H_2SO_4 (volume not stated), oxidising the $FeSO_4$ to $Fe_2(SO_4)_3$ with $KMnO_4$, and the Cr_2O_3 to CrO_3, by adding as much again of that reagent as is required to oxidise the iron, filtering off the Mn precipitate, and titrating the chromic filtrate after the addition of ferrous salt with $K_2Cr_2O_7$.

It was brought to our notice when analysing very low chrome steels that our results were invariably too high, and on investigation it was found, if a sample of bar iron were treated precisely as if Cr were present, on titrating that the number of c.c. K_2CrO_7 used was less than required by the ferrous salt added; this difference calculated out indicated a certain percentage of Cr. It then became customary to subtract this "blank" from our results. It was also found that the value of the "blank" varied with (1) the volume of acid taken to dissolve in (2) the excess of $KMnO_4$.

Influence of Acid.—Two grms. of steel, one free from and the other containing about 2 per cent, were dissolved in 100, 75, 50, and 30 c.c. respectively of H_2SO_4, boiled down till white sediment formed, taken up in boiling water, and finished in the usual way—with this exception, that only 0·125 grm. $KMnO_4$ was added in excess.

Table I.

Acid to dissolve.	Excess $KMnO_4$.	Blank. P.c. Cr.	Steel.	Steel minus blank.
100 c.c.	0·125 grm.	0·08	2·15	2·07
75 ,,	,, ,,	0·06	2·13	2·07
50 ,,	,, ,,	0·05	2·08	2·03
30 ,,	,, ,,	Nil	2·04	2·04

Analysed by Stead's modified acid permanganate, hypoaceto, and Arnold's phosphate, the average = 2·06 per cent Cr.

Influence of Excess $KMnO_4$.—Two grms. of bar iron treated as in Table I.

Table II.

Acid to dissolve.	Excess $KMnO_4$.	Blank, p.c. Cr.
30 c.c.	0·125 grm.	Nil
30 ,,	0·50 ,,	Nil
100 ,,	0·125 ,,	0·08
100 ,,	0·50 ,,	0·15
100 ,,	1·00 ,,	0·17

Next are given the results of a few chrome steels treated as in Table II.

Table III.

Mark.	Acid.	Excess $KMnO_4$. Grm.	Steel.	Steel minus blank.	P.c. Cr in ppt.	Total p.c. Cr.	
M	30	0·125	2·19	2·19	Nil	2·19	Stead's acid
	30	0·50	2·15	2·15	0·03	2·18	Permanganate
	100	0·125	2·32	2·24	Nil	2·24	= 2·20
	100	0·50	2·31	2·16	0·04	2·20	
W	30	0·125	0·36	0·36	Nil	0·36	
	30	0·50	0·33	0·33	0·02	0·35	Do.
	100	0·125	0·43	0·35	Not done	0·35	= 0·37
	100	0·50	0·48	0·33	0·03	0·36	
H	100	0·50	2·21	2·06	0·02	2·08	Do.
	100	1·00	2·24	2·07	Not done	2·07	= 2·09
S	30	0·50	0·78	0·78	,,	0·78	Do.
	100	0·50	0·91	0·76	,,	0·76	= 0·78

The Cr in the precipitate was determined by dissolving in HCl, making up to 250 c.c., boiling till free from Cl, and titrating as usual.

Thus it is clearly seen how the method, in the hands of different chemists, may, through a lack of definite instruction, yield varying results—more particularly noticeable in low chrome steels.

It is probable that the "blank" is due to a reaction between the excess of acid and $KMnO_4$, whereby some of the precipitate, which is somewhat soluble, is made active to ferrous salt. It was found on boiling some well washed precipitate in dilute acid, that the proportion thus active was small compared to the total amount dissolved.

The Laboratory,
Messrs. Thos. Firth and Sons, Limited,
Sheffield.

Preparation and Etherification of Dissymmetrical Dimethylsuccinic Acid.—E. E. Blaise.—The author finds that, in the case of succinic acid, the two carboxyls are not etherified simultaneously; that when the molecule is dissymmetrical, the two acid functions have very different values; the tertiary carboxyl being much more difficult to etherify than the primary. By this method it is very easy to decide whether the substituted succinic acid is symmetrical or not, and that there is not a constant relationship between the weights of the acid and neutral ethers formed at different moments of the reaction. —*Comptes Rendus*, cxxvi., No. 10,

THE CYCLICAL LAW OF THE ELEMENTS.

By THOMAS BAYLEY, Assoc. R.C.Sc.

When the elements are arranged in a line in the order of their atomic weights, it is apparent that there is from Li to F an orderly transition from the intensely positive alkali-metal type to the intensely negative halogen type, and then a sudden reappearance of the positive type in Na, after which there is a second orderly transition to the negative type (Cl), and then another change to positivity (K). Up to this point, therefore, two complete cyclical changes have been established, the first cycle from Li to Na—in all its essential details—being analogous with the second from Na to K. If then we proceed with the lineal arrangement, it is clear that we must first of all look for transitions and for reappearances of the alkali-metal type; in other words, for the continued development of the cyclical arrangement. And since analogous but modified transitions actually recur, and halogens followed by alkali-metals reappear, it is evident that the law of progression is actually cyclical. The first and fundamental feature of atomic progression is a progression in cycles.* The Li—Na cycle is a cycle involving the seven elements, Li, Be, B, C, N, O, and F, and the Na—K cycle involves also seven elements; and for this reason, and because in the succeeding cycles analogous groups of seven elements are repeated, almost all tabular expressions of the atomic progression have been set in a septenary form. But these arrangements, by unduly emphasising the septenary character of the periodic change, have perhaps somewhat obscured the more important and fundamental cyclical features of the progression. Before attempting to substantiate this assertion, however, it is necessary to consider the nature of the higher cycles which are complex, and to show that the properties of any element are more profoundly modified by position in the cycle than by position in the septenary series.

Assuming that hydrogen is the first element of an incompletely known cycle which we may call the first, then the Li—Na cycle becomes the second and the Na—K cycle becomes the third. Beyond this point the cycles are complex, and the fourth contains seventeen elements, of which the first, K, is completely analogous with Na; the second element, Ca, with Mg; and the third, Sc, with aluminium; for Na and K both conform to the alkali-metal type, Ca and Mg to the alkaline earth metal type, and Al and Sc to the type of the earth metals. But the analogies between Si and Ti, and between P and V, are less perfect, while the analogies between O and Cr and between Cl and Mn are very much less pronounced. The analogies between the latter pairs, indeed, appear to consist chiefly in structural resemblances between the compounds of the respective elements, due to the valency or atomicity impressed upon the septenary series as a primary law of its formation. The analogies between the elements of the septenary series entirely constituting the second and third simple cycles, and the elements constituting the first portion of the fourth cycle, a compound cycle, are perfect therefore only in the first, second, and third elements of each series respectively, and become fainter in the later members. Now the elements between which complete analogy exists are those which have analogous positions in the cycle, and the elements between which incomplete analogy exists are those which have not analogous cyclic position, but merely analogous serial position. The region of the third cycle — occupied by Na, Mg, and Al—corresponds to the region occupied by K, Ca, and Sc in the fourth cycle; for each group of elements occupies the front portion of its cycle, whereas Si, P, and S in the third cycle occupy a region posterior to the point of lowest atomic volume, while Ti, V, and Cr occupy a region anterior to the point of lowest atomic volume in the fourth. Neglecting for the moment the

* Bayley, *Phil. Mag.*, Jan., 1882,

position and properties of the three intermediate elements, Fe, Ni, and Co, and passing to the consideration of the second septenary series, which completes the fourth cycle, and to comparison of this with the third cycle, we see that analogy fails, or is chiefly structural, between Cu and Na, between Zn and Mg, between Ga and Al, but becomes more pronounced between Se and S and perfect between Br and Cl. The structurally analogous Cu and Na have nothing in common except serial position, and the fully analogous Br and Cl have similar cyclic position; Cl fails to find a complete analogue in Mn which has not analogous regional position, but finds it in Br, because both occur at the end of the cycle. To make this clearer it is necessary to study more closely the architecture of the simple and complex cycles. The increment of atomic weight occupied by the series Li—Na is 15·98, the increment from Na to K is 16·05, the increment from K to Fe is 16·86, the increment from Cu to Rb is 22, the increment from Rb to Ru is 16·2, and the increment from Ag to Cs is 25·04. The increments for the series constituting the simple cycles, and for the series occurring in the first portions of the fourth and fifth cycles, is therefore about 16 (or 17), and the increment for the series occurring in the posterior halves of the fourth and fifth cycles is 22 and 25. If we proceed to consider the nature of the sixth cycle, we are met at the outset by a difficulty, for since no alkali-metal of higher atomic weight than Cs has yet been discovered, it is not easy to fix the upper limit of the cycle.

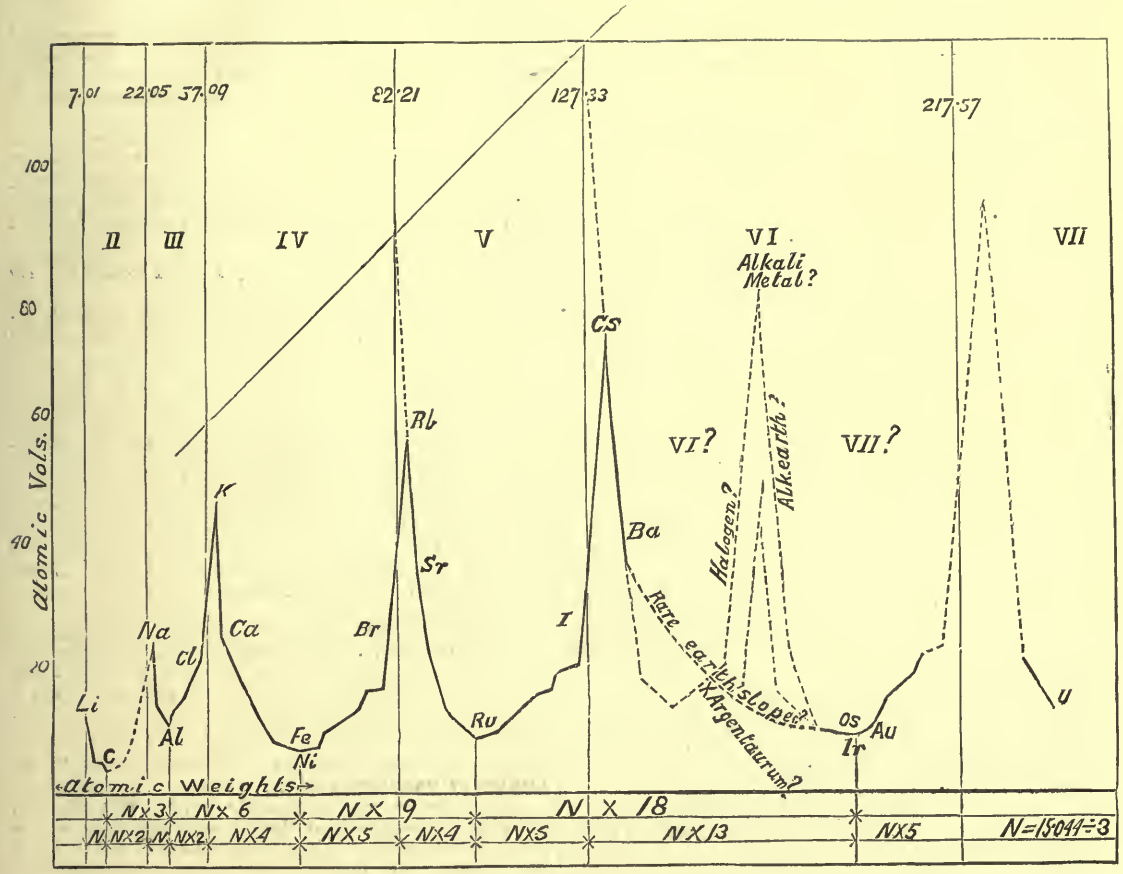
The usual arrangement of the elements in odd and even series, such as Mendeleeff's original classification or Brauner's modification of it, show three septenary series and an intermediate group between Cs and Os, and the increment of 57 in atomic weight corresponding to this space is just about what would be required for 24 elements. Commencing with K and writing its higher analogues in a line, we obtain the sequence K, Cu, Rb, Ag, Cs, in which each alkali metal is followed by a sub-family analogue, and, unless other conditions intervene in the sixth cycle, the unknown element of atomic weight c. 156 should be an analogue of Cu and Ag, and the unknown element of atomic weight c. 170 should be an alkali metal and the first member of a seventh cycle. But as every alkali metal is preceded by a halogen (neglecting the argon family), and succeeded by an alkaline earth metal, it also follows that the element of atomic weight 170 should be similarly accompanied. Reasoning also from analogy, we must suppose that the unknown halogen is somewhat less negative than I, because negativity decreases with atomic weight in the halogen family, and the unknown alkali metal and the alkaline earth metal must be more positive than Cs and Ba respectively, because positivity increases with atomic weight in the highly positive families. It also seems necessary, from analogy, to assume the existence of an intermediate group between 152 and 154. But in all other instances, both lower and higher, in the atomic progression the intermediate groups are preceded not by basic earth metals (such as Sm), but by elements such as Cr and Mn, Mo and (—c. 100), and Ta and W, which form oxides of a pronounced acidic character. If, therefore, there is a cycle stretching from Cs to the position of atomic weight 170, it must differ essentially from compound cycles below it and the compound cycle above it. We may now profitably turn to a consideration of the curves of atomic volume in the various cycles. It was first pointed out by L. Meyer that atomic volume has a periodic variation, and the curves given in the accompanying figure are essentially identical with those drawn in his "Modern Theories of Chemistry."

It is evident that atomic volume is a cyclical function. Each cycle, simple or compound, shows a loop, and all truly analogous elements occupy similar positions on the curves. The alkali metals have high atomic volumes, and occupy the top of the curves; the alkaline earth metals invariably occur on the downward flanks. The earth metals occur lower down on the same flank, and in the fourth and fifth angles they immediately precede the elements (Ti, V, Cr, Mn), (Zr, Nb, Mo, —), which form acidic oxides. The intermediate groups occupy the troughs of the curves, and the series Cu—Br, Ag—I, Au—Bi occur on the rising posterior portion of the curves. If, then, the element of atomic weight c. 170 is an alkali metal, it is reasonable to conclude that it has a high atomic volume, and that the curve of atomic volume indicated by the upper dotted line must exist, even if it does not follow—however probable it may appear—that this curve need necessarily be as steep as it is drawn. The curves of atomic volume present very remarkable regularities, using the word curve to mean the collection of straight lines drawn from point to point. Thus the lines drawn from Cl to K, from Br to Ru, and from I to Cs, are almost exactly parallel, as are some other lines of similar character.

In the earlier diagrams, before the atomic volume of Cs was determined, the line from I to Cs was assumed to occupy a position in accordance with this parallelism, and the facts when determined justified the assumption, and for these reasons it seems permissible to use this method of drawing parallel lines as a means of forecasting the atomic volumes of elements as yet undiscovered. Now, whether we draw the upper or the lower dotted curve, in which latter case the metal (atomic weight c. 170) would not be a perfect analogue of Na and K, it appears necessary to believe in the existence of a halogen and an alkaline earth metal, and also of a group of intermediate elements of the iron or platinoid type, followed by a series commencing with a true analogue of copper and silver. It is a significant fact that, although a number of elements are assigned to positions between atomic weight 150 and the atomic weights of Ta and W, there has as yet been described no element corresponding to the hypothetical intermediate group, or to the supposed halogen, alkali-metal, or alkaline earth metal. On the other hand, the numerous elements between atomic weight 150 and Ta which have been described are elements of a purely earth-forming type, separable from well-located earths, such as Sc, Yt, and La, which they closely resemble only by repeated fractional precipitations or similar methods. So far research has not rendered it possible to assign definite atomic weights to the majority of these rare earth metals, and much of the brilliant laborious work done upon them by Crookes and others has tended rather to bewilderment, yttrium and samarium, and several other rare earth metals, having been shown to be complex bodies; but accepting the usual location of these metals provisionally, it would seem that Tb>Er>Tm>Yb fall just where the hypothetical alkali-metal of atomic weight c. 170 would require to be placed, and that with these four elements there is a regular but small progression from greater to less basicity in the order given, which is what we might expect if the sixth cycle stretches from Cs to about atomic weight 233 with a long flank on the anterior (descending) portion of its curve of atomic volume occupied by a series of rare earth metals. This conception of the cyclic progression eliminates the unsymmetrical dotted curve, and substitutes a cycle of approximately symmetrical dimensions. The cyclical increments then appear as—

Cycle II.	Cycle III.	Cycle IV.	Cycle V.	Cycle VI.
c. 16	c. 16	46 (3×16)	47 (3×16)	94 (6×16)

and the position of lowest atomic volume, which in the lower cycles occurs near the middle of the curve, occupies in the sixth cycle a position nearer to the end. In these measurements of the length of the cycles, we have taken the increments of atomic weight from one alkali metal to the next higher in progression, but it does not necessarily follow that this is the proper method. For if the elements have been produced, as was suggested by Sir William Crookes, during the cooling of some primal form of



matter—the protyle,—we may imagine that after the genesis of each cycle had been completed, and the halogen had been formed, there came a turning-point in the evolution, probably marked by the development of an element of the argon type, after which the course of atomic genesis again set in the direction of alkali metal formation. If so, then clearly the cycle commenced at this turning-point, but the first element of the new series may not have been formed immediately. The conditions at the commencement of the cycle may not have permitted of the coherence of the newly condensed material into the atomic form, and the first element of the new cycle may, as it were, have had to wait until the attractive force of the condensed protyle had time to gather. Some such conception might explain a lateness in the appearance of an element like argon, endowed with little or no affinity; for if the element were all the while forming in a kind of nebulous intermediate condition, and if, as it appears, atomic weight is a function chiefly or wholly of the temperature at the moment of atomic formation, such an element might not take the atomic form until after the commencement of the next cycle. This, however, assumes some sort of connection between the attraction of the primal molecules for each other and the chemical affinity of the completed atom. Before we can attempt to fix the true dimensions of the cycles in accordance with this hypothesis, we must cast about for evidences of definite arithmetical dimensions in other regions of the cycles than the beginnings. The point of lowest atomic volume seems to be another definite turning-point in the cyclic changes; and taking carbon as representing this point in the second cycle, and iridium the similar point in the (large) sixth, we get an interval of atomic weight of 180·5. Dividing this by 12 we obtain 15·04, and adding this number to the atomic weight of carbon (11·97) the sum is 27·01, the atomic weight of aluminium (27·02), the element of lowest atomic volume in this cycle. By adding to aluminium (27·01) the expression 15·04×2, we obtain 57·09, which is between iron (55·9) and nickel (58·6), and the addition of 15·04×2 again gives 102·24, which is very near the atomic weight of ruthenium (102·7); and adding 15·04 × 6 to 102·24 gives 192·48, which is the atomic weight of iridium. Now, assuming this dimension 15·04 to represent the true dimension of a simple cycle, and adding it to lithium, we have 7·01+15·04=22·05, between fluorine and sodium, as the initial or turning-point for Cycle III. In like manner, 22·05+15·04 gives 37·09, between chlorine and potassium, as the initial-point of Cycle IV.; 37·09+15·04×3 gives 82·21, between bromine and rubidium, for the corresponding point of the fourth cycle, and 82·21+15·04×3 gives 127·33, between iodine and cæsium for the sixth cycle. If the sixth cycle is a large cycle 127·33+15·04×6 indicates 217·57 as its probable terminating point. If the cyclic dimensions be fixed in this manner, the point of lowest atomic volume in the various cycles occurs in the 2nd or 3rd at the one-third ($\frac{1}{3}$) distance, and in the 4th and 5th at the four-ninths ($\frac{4}{9}$) distance from the initial-point of the cycles. Thus—

$$\text{Li } 7{\cdot}01 + \frac{15{\cdot}04}{3} = 12{\cdot}01 \text{ (C = 11·97)}$$

$$22{\cdot}05 + \frac{15{\cdot}04}{3} = 27{\cdot}02 \text{ (Al = 27·01)}$$

$$37{\cdot}09 + \frac{15{\cdot}04}{3} \times 4 = 57{\cdot}13 \text{ (Fe = 55·9; Ni = 58·6)}$$

$82{\cdot}21 + \frac{15{\cdot}04}{3} \times 4 = 102{\cdot}25$ (Ru = 102·7)

$127{\cdot}33 + \frac{15{\cdot}04}{3} \times 13 = 192{\cdot}46$ (Ir = 192·5)

It may be assumed that the actual turning-point of lowest atomic volume may not be occupied by an element having the atomic weight corresponding to the temperature existing when the evolutionary crisis arrived.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 17th, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

(Concluded from p. 150).

*38. "*Contributions to the Chemistry of Thorium.*" By BOHUSLAV BRAUNER, Ph.D.

As there are few direct methods of separating the elements of the rare earths, the author investigated the reaction of Bahr (1864), who showed that thorium oxalate is easily soluble in a solution of ammonium oxalate. Bunsen (1876), though he found that the oxalates of the other rare earths are only slightly soluble in that reagent, had to repeat the process of solution many times to obtain a product which did not show in its spark spectrum the lines of other elements.

The reaction is due to the formation of a double thorium-ammonium oxalate, decomposed by water, and existing in solution only in the presence of free ammonium oxalate. After numerous crystallisations, a salt was obtained having the formula—

$$Th(C_2O_4)_2+2(NH_4)C_2O_4+4H_2O,$$

with one-third to one-half of free $(NH_4)_2C_2O_4 + H_2O$. Finding, however, that the solution readily becomes supersaturated, a compound having the formula—

$$Th(C_2O_4)_2+2(NH_4)C_2O_4+7H_2O,$$

was obtained in such a high state of purity that from its analysis the atomic weight of thorium, Th = 232·59, could be calculated.

This "complex" salt is ammonium thoroxalate. It is decomposed by water, but a definite quantity of the soluble product of decomposition dissolves the insoluble constituent, so that one part of water keeps one part of ammonium thoroxalate in solution if an additional half-molecule of free ammonium oxalate is present. The salt forms two hydrates, in accordance with Potilizin's law that a compound forming supersaturated solutions exists in several hydrate forms, one with $7H_2O$, the other with $4H_2O$. The former loses water in air of average humidity, passing into the latter form, which becomes anhydrous in perfectly dry air, or more readily at 100°, without loss of ammonia. On heating at higher temperatures, large quantities of cyanogen gas are evolved.

The amount of the decomposition of the salt caused by increasing the quantity of water was determined, together with the proportion of ammonium oxalate required to prevent decomposition. Three mols. of ammonium oxalate form, with 1 mol. of thorium oxalate, a clear solution in 300 mols. of water. This solution is, however, supersaturated with thorium oxalate, the latter separating until their relative proportions become 3·3 : 1. A convenient method for the purification of thorium may be based on these results, as the author has determined quantitatively the great difference in solubility between the oxalate of the feebly basic tetravalent thoria and those of the other trivalent rare earths in ammonium oxalate. The rule was thus established: "the tendency to form complex oxalates is inversely proportional to the basicity of an earth." This, and another property of oxalates, that their stability under the oxidising action of nitric acid decreases considerably with an increasing basicity of the earth, was utilised for the purification of thorium.

On precipitating a solution of ammonium thoroxalate with oxalic acid, an acid thorium oxalate—thoroxalate of thorium and hydrogen—is formed, having the formula $H_2Th_2(C_2O_4)_5+9H_2O$. On using mineral acids (Glaser, *Zeit. Anal. Chem.*, 1897, xxxvi., 216; 1898, xxxvii., 25), a different result is observed.

*39. "*On the Atomic Weight of Thorium.*" By BOHUSLAV BRAUNER, Ph.D.

The author determined the purity of the material, obtained, as described above, by the spark spectrum, and by atomic weight determinations. He determined in the air-dry oxalate (*a*) the thorium tetroxide by heating, and (*b*) the percentage of C_2O_3 by means of a solution of potassium permanganate. The first series of experiments gave concordant results, leading to the value Th = 233·3, a value not in agreement with that previously obtained by him, Th = 232·59. Further study showed that the oxalate used was contaminated with basic salt, and, a normal oxalate being prepared, the following values were obtained as a result of five series of experiments made with different preparations:— Th = 232·50, 232·46, 232·45, 232·31, 232·33, 232·50, 232·44, and 232·35; average, Th = 232·42.

This number agrees with that obtained by Krüss and Nilson, Th = 232·45. The author then investigates the conditions which led him to obtain the high value in the first series, approaching the value of Clève, Th = 234·5. The work of other investigators is vitiated by untrustworthy methods and impure material.

*40. "*On the Compound Nature of Cerium.*" By BOHUSLAV BRAUNER, Ph.D.

The author showed in 1882 (*Trans.*, xli., 68; *Monats.*, iii., 486) that cerium from cerite is associated with an element whose higher oxide forms yellow and lower white salts, though the higher oxide is far less stable than cerium tetroxide. The substance is found with lanthanum and didymium when separating cerium by Bunsen's method. In 1885 the author showed (*Trans.*, xlvii., 879) that the substance remains in the mother-liquor after the bulk of the cerium sulphate has crystallised, and may be precipitated from it by alcohol. Schützenberger has repeated the author's experiments without mentioning his name. After applying Debray's method of separating cerium to these fractions and again fractionating, the author obtained substances with the following values for the atomic weights. The method employed was the analysis of the oxalate, and the determination of "active" ozonic oxygen by Bunsen's method in the oxide obtained by calcination, the latter number being given in parenthesis:— R''' = 140·25 (4·64), 140·22 (4·65), 140·12 (4·81), 140·00 (4·65), 140·01 (4·59), 139·65 (4·61), 139·16 (4·01), 138·72 (4·51), 136·50 (3·31), 135·43 (3·93), 132·07 (3·73), 130·70 (3·21). As the value of the atomic weight decreases, the colour changes from white to a reddish brown orange.

The quantity of "active" oxygen, therefore, decreases almost in proportion to the decrease in value of the atomic weight. If we assume that the "active" oxygen is due entirely to the cerium present, the value of the atomic weight of the other element may be calculated at about 110. The author has thoroughly investigated the spark spectrum of the lower fractions, but has found no characteristic line other than those of cerium. In one case only were traces found of the two characteristic groups of lines in the red belonging to yttrium, No appreciable amount of yttria could be found, however, in the solution, even when a large quantity of the material in question was treated with potassium sulphate. As terbium forms a higher oxide of an orange colour, the colour of

the lower fractions of cerium may be due to its presence, but, as its atomic weight is higher than that of cerium, another earth of lower atomic weight must still be present, and it is not improbable, that, like gadolinium, this element may give no characteristic spectrum. The recent controversy between Wyrouboff and Boudouard (*Comptes Rendus*, 1897, cxxv., *pass.*) has led the author to publish the result of this research, which has occupied him many years.

*41. "*On Praseodidymium and Neodidymium.*" By BOHUSLAV BRAUNER, Ph.D.

Applying Mendeleeff's method of crystallisation of the double nitrates with ammonium nitrate to a mixture of lanthanum and didymium, Auer von Welsbach (1885) succeeded in splitting up the old didymium into "praseodym" and "neodym." Praseodidymium, according to him, has an atomic weight Pr = 143·6, and forms two oxides, Pr_2O_3 and Pr_4O_7. The higher oxide is black-brown, the lower forms green salts with a characteristic spectrum. Neodidymium, Nd = 140·8, gives only one oxide, Nd_2O_3 with pink salts possessing eleven absorption bands. Nothing of importance has been added to our knowledge on the subject during the last eleven years.

The author spent several years in repeating Welsbach's work, but last year he obtained from Dr. Waldron Shapleigh, in Gloucester, N.J., a quantity of highly purified research material.

From this mixture (40 grms. of praseodidymium oxide with 20 grms. of lanthanum oxide) the latter was removed, the former being converted by fusion with nitre into the oxide Pr_2O_4. This was purified by fractionating with ammonium nitrate solution, ammonia, and oxalic acid.

A preliminary determination of the atomic weight gave the value Pr = 140·8. The analysis of the oxalate and the synthesis of the sulphate gave thirteen numbers, varying between 140·84 and 141·19, the average being Pr = 140·95. The lower oxide, Pr_2O_3, is of a beautiful pale green colour, and the spectrum of its green salts contains the absorption bands λ = 5968, 5895, 4812, 4693, and 4447 (Rowl.). Praseodidymium trichloride gives a characteristic spark spectrum.

Salts of the trioxide having the following formulæ have been prepared and analysed by the author:—

$$Pr_2(SO_4)_3,\ Pr_2(SO_4)_3+6H_2O,\ Pr_2(SO_4)_3+8H_2O,$$
$$Pr(NO_3)_3+2NH_4NO_3+4H_2O,\ PrAc_3+H_2O,$$
$$Pr_2(C_2O_4)_3+10H_2O.$$

According to Professor Vrba's measurements, the salt $Pr_2(SO_4)_3+8H_2O$ is isomorphous with $Y_2(SO_4)_3+8H_2O$ and other sulphates of this type. This fact, and the slight solubility of the oxalate in ammonium oxalate, prove that the formula of the lower oxide is Pr_2O_3, and not Pr_2O_4 or Pr_2O_5, in which cases the atomic weight would be 188 or 235. The tetroxide, Pr_2O_4, obtained from the nitrate on heating to a temperature of 440°, or by fusion with nitrate at 400°, is jet-black, but it becomes dark brown in a state of fine division.

Up to the present, only its basic salts have been obtained; the sulphate $2Pr_2O_4 \cdot SO_3+2\frac{1}{2}H_2O$, and the basic acetate in acetic acid solution, having a formula which may be represented by either $Ac_3—Pr^{IV}O—Pr^{IV}—(OH)_3$, or $Ac_2—Pr^{III}{}_2O_2—OH.Ac+H_2O$. The double fluorides are being investigated.

It is of the greatest importance to know whether the tetroxide is (*a*) a true oxide of the water type, with ozonic oxygen (like lead) tetroxide, PbO_2, in which case the praseodidymium would be tetravalent, or (*b*) a true peroxide of the hydrogen peroxide type, with antozonic oxygen (like barium peroxide, BaO_2), in which case the metal would be trivalent. With regard to the first view, it yields, with dilute acids, free oxygen, and the solution does not reduce potassium permanganate (negative test for hydrogen peroxide). On treatment with concentrated nitric and sulphuric acids, oxygen containing much ozone is evolved, and with hydrochloric acid chlorine is set free, arising probably from the decomposition of the unstable perchloride, $PrCl_4$ (?). Like other ozonic oxides of the water type, it presents with hydrogen peroxide the phenomenon of catalysis in the presence of dilute sulphuric acid, a quantity of the hydrogen peroxide being oxidised, strictly equivalent to the "active" oxygen lost by praseodidymium tetroxide according to the equation—

$$Pr_2O_4+H_2O_2+3H_2SO_4+Aq=$$
$$=Pr_2(SO_4)_3+O_2+4H_2O+Aq.$$

On the other hand, praseodidymium tetroxide gives with ether, water, sulphuric acid, and potassium bichromate an intensely blue colouration (Baresville's reaction) according to the equation—

$$Pr_2O_4+3H_2SO_4+Aq=Pr_2(SO_4)_3+H_2O_2+2H_2O+Aq.$$

In the treatment, therefore, of the tetroxide with dilute sulphuric acid, both reactions take place simultaneously, and the result is the evolution of oxygen,—

$$2Pr_2O_4+6H_2SO_4+Aq=2Pr_2(SO_4)_3+O_2+6H_2O+Aq.$$

Praseodidymium tetroxide is, therefore, an oxide of a new kind, belonging simultaneously to the ozonic oxides of the water type, and to the antozonic oxides of the hydrogen peroxide type; it is, in fact, the missing link between these two hitherto entirely different types of peroxides, its active oxygen being at the same time both entirely ozonic and entirely antozonic.

The basic acetate of the tetroxide, which is nearly white, and in the spectrum of which the blue absorption bands are invisible when seen by reflected light, though the yellow band remains unchanged (an indication of the complex nature of praseodidymium), is the salt of an oxide belonging to the hydrogen peroxide type, for it reduces permanganate quantitatively, and gives Baresville's reaction for hydrogen peroxide. It is, however, so remarkably stable that it does not part with all its active oxygen, even after being boiled for an hour with concentrated caustic potash solution.

As regards the author's neodidymium, its absorption spectrum contains the bands λ = 7283, 7080, 6905, 6368, 6279, 6247, 5788, 5323, 5211, 5097, 5063, and 4280. It contains, in addition to these, a strong sharp band of wave-length λ = 4694, which differs in character and position from the praseodidymium band λ = 4693. There were also traces of Pr 4812 and Pr 4447, Dy 4752 and 4605 (Sm. series ?).

The value of the atomic weight of neodidymium found after the first purification of the material by treatment with oxalic acid was Nd = 143·4, after another purification Nd = 143·63. Its lower oxide, having the formula Nd_2O_3, is of a beautiful pink colour with an amethyst tint, whereas the higher oxide contains a little more oxygen than corresponds to the formula Nd_2O_5 (the author's old Di_2O_5). Neodidymium also gives two series of salts, the acetate of the higher oxide being nearly white. According to a quantitative analysis, by comparing the intensity of the bands the author's neodidymium contained 2·9 per cent praseodidymium, whereas the old didymium from cerite contained in 100 parts of the oxide 78·8 parts Nd_2O_3 and only 21·2 per cent Pr_2O_3.

With regard to the position of these elements in the periodic system, the author concludes, from the tendency of them both to become more highly oxidised than would correspond to the formulæ Pr_2O_4 and Nd_2O_5, that praseodidymium and neodidymium may be further split up. This is regarded as very probable by all rare earth chemists. The pure oxides will probably be found to have the formulæ Pr_2O_5 and Nd_2O_6, so that the eighth series of the periodic system would assume the following form:—

I.	II.	III.	IV.	V.	VI.
Cs.	Ba	La.	Ce.	Pr.	Nd.
133	137·4	138·2	139·7	141	143·6.

Discussion.

The President congratulated Professor Brauner on the valuable scientific results he had presented to the Society, and on behalf of the members expressed their appreciation of the motives which had induced the author to come all the way from Prague to communicate four papers of such great importance to the Chemical Society. He wished him success in the continuation of such laborious and intricate investigation.

42. "*Action of Ammonia and Substituted Ammonias on Acetylurethrane.*" By George Young, Ph.D., and Ernest Clark.

Acetylurethane has been subjected to the action of ammonia and of substituted ammonias under varying conditions as to solvent, temperature, and pressure. The general results of the investigation show that action takes place principally according to the equation—

$$MeCONHCO_2Et + NH_2R = MeCO{\cdot}NH{\cdot}CO{\cdot}NHR + EtOH.$$

Under certain conditions the products point to the action having resulted in the formation of acetamidine urethanes,—

$$MeCO,NHCO_2Et + NH_2R = Me(NHR)C{:}N{\cdot}CO_2Et + H_2O.$$

These acetamidines have not been isolated, but in their place the products of hydrolysis, acetamide and substituted acetimides, have been obtained,—

$$Me(NHR)C{:}N{\cdot}CO_2Et + 2H_2O = Me{\cdot}CO{\cdot}NHR + NH_3 + CO_2 + EtOH.$$

Ammonia and methylamine enter into action most easily, piperidine, aniline, the naphthylamines, and phenylurea less so. Acetylurea, acetanilide, and diphenylamine appear to be without action.

43. "*Formation of Oxytriazoles from Semicarbazides.*" By George Young, Ph.D., and Benjamin Mitchell Stockwell, B.Sc.

This paper contains an account of the formation of of oxytriazoles according to the equation—

$$R{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 + C_6H_5{\cdot}CHO + O = R(C_6H_5){\cdot}C_2N_3OH + 2HO,$$

where R is an aromatic radicle. The following substances are described:—*Paratolylsemicarbazide*, m. p. 187–188°. *Acetylparatolylsemicarbazide*, m. p. 212·5°. *Benzoylparatolylsemicarbazide*, m. p. 218°. *Paratolylazocarbamide*, m.p. 142°. *5-Phenyl-1-paratolyl-3-oxytriazole*, m. p. 242°. *Acetylphenylparatolyloxytriazole*, m. p. 112—113°. *Benzoylphenylparatolyloxytriazole*, m. p. 132°. *Phenylparatolylethoxytriazole*, m.p. 51—52°. *β-Naphthylsemicarbazide*, m.p. 225°. *Phenyl-β-naphthyloxytriazole*, m. p. 274—275°. *Acetylphenyl-β-naphthyloxytriazole*, m.p. 142—143°. *Benzoylphenyl β-naphthyloxytriazole*, m. p. 141—142°. *Metanitrophenylsemicarbazide*, m.p. 195°. *Benzoylmetanitrophenylsemicarbazide*, m. p. 188—189°. *Metanitrophenylazocarbamide*, m. p. 168—169°. *5-Phenyl-1-metanitrophenyl-3-oxytriazole*, m. p. 235°. *Acetylphenylmetanitrophenyloxytriazole*, m. p. 130—132°. *Benzoylmetanitrodiphenyloxytriazole*, m. p. 168°. *Nitrodiphenylethoxytriazole*, m. p. 96°.

44. "*Formation of aa'-Dihydroxypyridine.*" By S. Ruhemann, Ph.D., M.A.

Ethylic *aa'*-dihydroxydinicotinate (*Proc.*, 1898, xiv., 47) when boiled with concentrated hydrochloric acid, yields the hydrochloride of *aa'*-dihydroxypyridine, from which ammonia sets free the base m. p. 192—193°. The same substance is obtained from Guthzeit and Dressel's monethylic ethoxypyridone dicarboxylate (*Annalen*, 1891, cclxii., 113) by boiling hydrochloric acid.

45. "*Position-isomerism and Optical Activity; the Comparative Rotatory Powers of Diethylic Mono-benzoyl and Mono-toluyl Tartrates.* By Percy Frankland, F.R.S., and J. McCrae, Ph.D.

The authors review the present state of knowledge concerning the relative rotatory powers of the phenyl and three toluyl derivatives of optically active compounds, and point out that, whilst of the three isomeric toluyl groups the ortho- has almost invariably the least and the para- the greatest rotatory influence, the rotatory influence of the phenyl group is in some series greater, and in some less, than that of any one or of all of the toluyl groups.

As a contribution to this study, the authors have prepared the compounds mentioned above, and have determined their rotations in a fused state over a wide range of temperature, whilst they have also determined the molecular weight and rotation of each in glacial acetic acid solution, with a view of ascertaining the relative rotations of the compounds in the monomolecular condition.

The following are the specific rotations at 100° for each of the compounds, as well as of diethylic tartrate, from which they may be regarded as derived.

Diethylic tartrate	$[\alpha]_D$ 20° = + 7·66°	$[\alpha]_D$ 100° = +15·77°
Diethylic mono-benzoyltartrate	$[\alpha]_D$ 24° = +20·71°	$[\alpha]_D$99·5° = +17·69°
Diethylic mono-*o*-toluyltartrate	$[\alpha]_D$ 20° = +11·82°	$[\alpha]_D$ 100° = +10·88°
Diethylic mono-*m*-toluyltartrate	$[\alpha]_D$ 20° = +13·59°	$[\alpha]_D$ 100° = +12·57°
Diethylic mono-*p*-toluyltartrate		$[\alpha]_D$ 100° = +15·85°

Thus the dextrorotation of diethylic tartrate increases with rise of temperature, whilst that of the above monacidyl tartrates diminishes. In glacial acetic acid solution, the benzoyltartrate has a lower rotation than the para-toluyltartrate, but otherwise the above order of the rotations is unchanged. In all cases the rotation in glacial acetic acid solution was considerably lower than that of the pure substance, but this difference is not attributable to the pure substance in the fused state being dissociated, for the rotation of the diethylic monobenzoyltartrate in benzene solution was even lower still, and yet in benzene solution it is more probable that there would be association than in glacial acetic acid. Thus from the results in benzene it would appear that association of the benzoyl compound is attended with diminution in the rotation, so that the higher rotation of the liquid benzoyl compound itself cannot be due to association also. Neither do the molecular volumes of these compounds point to association when interpreted by Traube's formula.

Diethylic monobenzoyltartrate has been previously prepared by Guye and Fayollat (*Bull. Soc. Chim.*, 1895, [3], xiii., 201); their preparation was admittedly impure, and yielded a very much lower rotation and melting-point. It was first prepared by Perkin (*Trans.*, 1867, xx., 138), but without determining the rotation, the melting-point which he obtained was almost exactly the same as that found by the authors.

46. "*The Action of Di-isocyanates upon Amido-compounds.*" By H. Lloyd Snape, D.Sc., Ph.D.

By the action of diphenylene di-isocyanate upon phenylhydrazin in ethereal solution, *diphenylenediphenylsemicarbazide*,—

$$Ph{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}Ph,$$

was obtained. The product was a white powder which was insoluble in the more common organic solvents. It gave with copper sulphate a chocolate-brown colour, which was changed to green on the addition of ammonia.

Toluylenediphenylsemicarbazide,—

$$Me{\cdot}C_6H_3(NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}Ph)_2,$$

(1 : 2 : 4) was prepared by acting with 1 : 2 : 4-toluylene-di-isocyanate on an ethereal solution of phenylhydrazin. The product, after re-crystallisation from alcohol, consisted of colourless crystals which decomposed and rose in a capillary tube at 203°. This carbazide also was insoluble in the more common organic solvents, with the

exception of alcohol, in which it was difficultly soluble. With copper sulphate, it gave a wine-red colouration which changed to green on the addition of ammonia.

1:2:4-*Diphenyl-toluylene-diurea*,—

$$Me{\cdot}C_6H_3(NH{\cdot}CO{\cdot}NH{\cdot}Ph)_2,$$

was obtained on mixing ethereal solutions of aniline and toluylenediisocyanate. The product was re-crystallised from alcohol; it formed microscopic needles which melted at 261° with accompanying decomposition. It was difficultly soluble in methyl, ethyl, and amyl alcohol.

1:2:4-*Toluylene-diurea*, $Me{\cdot}C_6H_3(NH{\cdot}CO{\cdot}NH_2)_2$, was prepared by treating an ethereal solution of toluylenediisocyanate with ammonia and crystallising the product from water. Minute crystals, which melted with accompanying decomposition at about 252°. It was sparingly soluble in alcohol. Lussy had previously described this reaction, but states that the product melts at 220°.

47. "*The Action of Alkyl Iodides on Silver Malate and on Silver Lactate.*" By THOMAS PURDIE, F.R.S., and G. DRUCE LANDER, B.Sc.

The object of this research was to discover the cause of the abnormally high optical activity of the ethereal malates and lactates prepared by the silver salt method. An abstract of the first part of the paper treating of the action of isopropylic iodide and ethylic iodide on silver malate has already been published as a preliminary note (*Proc.*, 1896, xii., 219). The high activity of the malates, thus prepared, is due to the simultaneous production of ethereal salts of the much more active alkyloxysuccinic acids.

The silver salt of the inactive lactic acid acts in a similar manner. With isopropylic iodide, the ethereal salt of (*n*- or iso-) propoxypropionic acid is produced in considerable quantity. By reactions similar to those employed in the case of silver malate, the substance was separated from the ethereal lactate with which it is mixed, and identified by the analysis of several salts obtained from it. Evidence was also obtained that with ethylic iodide the ethylic salt of ethoxypropionic acid is produced, though in this case, as in the corresponding reaction with silver malate, it was not possible to isolate the salts in the pure state owing to the small quantity of the alkyloxy-acid formed. The authors have recently effected the resolution of several alkyloxy-propionic acids by means of alkaloids, and find that these acids are highly active as compared with lactic acid. Their production in the reaction above referred to accounts therefore for the abnormal activity of the ethereal lactates prepared from silver lactate.

The reaction seems to be a general one for the silver salts of hydroxy-acids (see following paper), and cannot therefore be relied on for the preparation of the ethereal salts of these acids in the pure state. With the permission of Mr. Brame, the authors have recently extended his experiments on the action of alkyl iodides on silver tartrate. The results already obtained point to the formation of dialkyloxysuccinates being the cause of the abnormally high activity of the ethereal tartrates thus prepared. The authors are carrying on the research with the view of throwing light on the reaction by which the alkyloxy-acids are produced, and of adapting it, if possible, for the direct preparation of optically active acids of this kind from the corresponding active hydroxy acids.

48. "*On the Optical Rotations of Methyl and Ethyl Tartrates.*" By J. W. RODGER and J. S. S. BRAME.

The authors, in attempting to prepare the alkyl tartrates in a high state of purity, find that when prepared by saturating an alcoholic solution of the acid with hydrochloric acid, or heating the acid or mono-substituted ester with alcohol in sealed tubes, the rotation of the product is much lower than that obtained for esters prepared by the action of an alkyl iodide on silver tartrate.

Differences of the same nature have been observed by J. Wallace Walker (*Trans.*, 1895, lxvii., 914) in the case of the lactates, and by Purdie and Williamson (*Trans.*, 1896, lxix., 818) for malates and lactates. With alkyl tartrates, however, the difference in activity is much greater than with lactates or malates. Further, the rotation for different specimens of tartrates prepared by the silver method is by no means constant, although every precaution was taken to ensure similar treatment during preparation.

In order to determine any other differences in the esters prepared by these different methods, samples of methyl tartrate giving these different optical activities were hydrolysed with excess of sodium hydrate, when the products of hydrolysis gave practically the same rotations. Secondly, no difference in the refractive indices was found; and on combustion of methyl and ethyl tartrates prepared by different methods and varying widely in rotation, no real difference in the percentage of carbon could be detected.

These abnormal results for the rotations may be explained on three hypotheses. The low rotation of the ethereal salts prepared by hydrochloric acid saturation or by the sealed tube method may be due to racemisation. Second, the esters from the silver salts may be isomeric with and more active than those prepared by other methods; or third, the esters prepared from silver salts may be contaminated with some much more optically active substance.

The first hypothesis is precluded by the constancy of the rotations obtained by the authors for specimens prepared by three different methods and the agreement with the rotations observed by others with these substances. The second is improbable, but receives some support from the result of hydrolysis. With regard to the third hypothesis, Purdie and Lander in a preliminary note on the action of alkyl iodides on silver malate (*Proc.*, 1896, xii., 221) ascribe the higher rotation given by the malates so obtained to the presence of "small quantities of the ethereal salts of the highly active alkyloxy-acids." The same explanation may hold with the tartrates, in which case these derivatives must be highly active, for they can only be present in small amount, since there is no appreciable rise in the percentage of carbon found. If the high rotation for tartrates prepared from silver salts is due to this cause, then the agreement of results obtained on hydrolysis is only a coincidence.

NOTICES OF BOOKS.

Agriculture in some of its Relations with Chemistry. By F. H. STORER, S.B., A.M., Professor of Agricultural Chemistry in Harvard University. In three volumes. Seventh Edition, revised and enlarged. London: Sampson Low, Marston, and Co. 1897. Pp. 1901.

AGRICULTURE being perhaps the most important industry in the world, for "The farmer feeds them all," it is with pleasure that we welcome another, the seventh edition of Professor Storer's valuable work. It differs from the previous editions in that it is printed in larger type, and necessarily from new plates; it has been entirely re-written, and a large amount of fresh matter has been interpolated.

Vol. I. is divided into thirteen chapters; the first four deal with the general relations of the soil, air, and water to plant life, and to each other, water being a subject of great importance as the means of bringing the plant-food to the plant, though some leaves can absorb ammonia from the air; the amount of ammonia present, however, is so slight that it cannot have much effect on the nourishment of the plant. Very striking results are said to have been obtained by placing lumps of solid carbonate of ammonium on the hot water pipes of a conservatory, so that the amount of ammonia in the air was increased to from 2 to 4 parts per 10,000 by weight.

The characters of different soils and their tillage occupy chapters v. and vi., after which we come to manures, soils considered as chemical-agents, and modes of action of special manures, such as gypsum or plaster-of-Paris, which is described as capricious and uncertain. It is recommended to be strewn with a liberal hand on moist places in stables and cow-stalls, as it checks the fermentation of the urine, thought it should not be added directly to the manure heap. Chapter x. deals with phosphatic fertilisers, and chapters xi., xii., and xiii., with the various assimilable nitrogen compounds.

Passing to Vol. II., which contains fourteen chapters, we begin with the question of nitrogenised animal and vegetable refuse, or the less easily assimilable kind; farm yard manure is of this class, and the effect of it is felt for three years, though two consecutive crops of wheat will exhaust it.

We now come, in chapter xv., to an entirely different subject, namely, symbiosis or blended growth. It is one of the commonest things in nature, whether in animal, fish, reptile, bird, or plant life, to find one species living with another. In the case of plants they are generally parasites. In this chapter we also find an interesting description of the root-nodules, which have recently been proved to fix nitrogen from the air and supply it to the plants. In chapter xvi. we read about the various conditions and functions of carbonic acid, and in chapter xvii. about green-manuring, the use of sea-weed as manure, &c. Humus or vegetable mould is a reservoir of nitrogen; it resists, decay, but little is known as yet as to its precise chemical composition. Its value as a manure depends upon several properties. First, no doubt, its power of supplying nitrogen to the plants; then because of its porosity it imbibes and holds water, by its lightness it improves many soils, it promotes chemical action in the soil both by means of the acids it contains and by those caused by its eventual decay. Chap. xxi. deals with the different methods of applying manure; the best method naturally seems to be to place it deep enough to get the capillary moisture, but not so deep that the air cannot gain access to it. In chap. xxiv. we come to potassic manures. It has already been shown that potash is essential for the life of plants; in fact, in ancient times potash was known as the "vegetable alkali" to distinguished it from soda, which was called the "mineral alkali." A great deal of the potash in soils comes from the decomposition of felspar; nearly all clays and clayey soils contain potash, and much is returned to the land from the crops, but the waste must be made up by potash salts of some kind, according to the kind of crops; for instance, chloride of potassium will not do for tobacco, as chlorides hinder its burning. There is a good deal of difference of opinion as to the use of lime as a manure. This matter, and a great deal more, bearing on the same subject is fully discussed in chap. xxvi.

Vol. iii. also contains fourteen chapters, the first of which, chap. xxviii., is historical and reviews the history of manures. Next come the theory of the rotation of crops, and special systems of rotation. One striking illustration of the significance of rotation is afforded by the so-called fairy-rings in old grass fields; they are really circles of grass of coarser growth and greener colour than the rest, and are caused by the growth of a fungus from a spore which happened to fall there; it grows, dies, and decays, and thus furnishes extra nourishment to the grass; after a time a new crop of fungus grows from the spores shed by the first lot, and so it gradually spreads.

The practice of rotation is not based upon chemical or botanical considerations, but is of great antiquity. In England and Germany, however, it took its rise from the village common-land system, where to avoid disputes the land was marked off into three great parts, one for winter grain, one for summer grain, while the third was left fallow; then each year (like Alice's tea-party) they shifted round one.

The important questions of irrigation and sewage are dealt with in chapters xxxii. and xxxiii. Historians can tell us that civilisation had its rise in irrigated countries. In Egypt, for instance, where we are in the habit of saying man first became civilised; though we think it highly probable that man had already been civilised long before in some other place. Peru, also a rainless country, was skilfully irrigated by the Incas. Strange to say, the art of irrigation suffered an unaccountable decline, and the result was always the downfall of the nation. Irrigation keeps the land sweet, and this is one of its principal merits.

A great deal of useful and interesting information is to be found in chap. xxv., on generalities as to the growth of crops. We then come to several chapters devoted specifically to barley, oats, and hay, and the establishment and maintenance of hayfields; and in chap. xxxix. we have the theory and practice of making hay. Turning the hay frequently prevents fermentation and waste.

The last chapter of this comprehensive work deals with ensilage. In recent years it has been found to be a great improvement to build the silo in the form of a high bin, in or near the barn, instead of digging holes in the ground as formerly practised. One difficulty in ensilage is to check fermentation: M. Mueller made a very successful experiment of using bisulphide of carbon as a germicide; a lot of grass which had begun to decay, together with a lot of buckwheat, sunflower plants, cabbage leaves, tops of beets, and some straw and chaff, were siloed, with bisulphide of carbon sprinkled on between the layers; when the silo was opened the fodder was found to be a compact, well-preserved mass, readily and greedily eaten by cattle, and all smell of the bisulphide had disappeared.

At the end of Vol. III. we find a copious and excellent index to all three volumes, and we must finally express our admiration for the excellent arrangement and masterly handling of the whole subject.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 10, March 7, 1898.

Chemical Actions of the Electric Discharge. The Aldehyds and Nitrogen.—M. Berthelot.—Continuing his experiments on the chemical action of the electric discharge, the author found it necessary to follow the comparative study of the fixation of the nitrogen in the aldehydic compounds. He gives a long list of experiments tried and results obtained with:—A. *Aldehyds of the Fatty Series:* (1) Ethylic aldehyd, C_2H_4O; (2) Primary propylic aldehyd, C_3H_6O; (3) Acetone, or secondary propylic aldehyd, C_3H_6O; (4) Dimethylic methylate, $C_3H_8O_2$. B. *Derivatives from the Aldehyds of the Fatty Series:* (1) Aldol, $C_4H_8O_2$; (2) Paraldehyd, $C_6H_{13}O_3$; Trioxymethylene, $C_3H_6O_3$; (4) A 60 per cent solution of CH_2O. C. *Aldehyds belonging to a less Hydrogenised and Cyclic Series:* (1) Camphor, $C_{10}H_{16}O$; (2) Benzylic aldehyd, C_7H_6O; (3) Benzoine, $C_{12}H_{12}O_2$; (4) Cinnamic aldehyd, C_9H_8O; (5) Salicylic aldehyd, $C_7H_6O_2$; (6) Furfurol, $C_5H_4O_2$; (7) Glucose, $C_6H_{12}O_6,H_2O$, and its derivatives. As a result of this large number of experiments, the author finds that, under the influence of the electric discharge, all the aldehyds examined fix nitrogen, forming condensed compounds, amides or amines; the fixation of the nitrogen does not cause so great a loss of hydrogen as in the case of carbides and the corresponding alcohols.

Chemical Action of the Electric Discharge. Organic Acids and Nitrogen.—M. Berthelot.—In this

paper the author describes his experiments on:—A. *The Monobasic Acids*, such as acetic, propionic, formic, &c. B. *The Monobasic Acids with a Simple Function:* Crotonic and benzoic acids. C. *Bibasic Acids with a Simple Function*, such as succinic, fumaric, phthalic, &c. D. *The Alcohol Acids*, lactic, malic, &c. E. *Acids with a Complex Function*, pyruvic, levulic, &c. He finds that, as a rule, the organic acids fix nitrogen in the same manner as the alcohols and the aldehyds. This fixation, in the case of acids, occurs without any loss of hydrogen. In the case of acetic and propionic acids, one molecule of acid fixed an atom and a half of nitrogen; the limit with higher acids has not been determined. No oxygen is lost in either the solid or liquid compounds.

Observations Relative to the Chemical Action of the Electric Discharge on Dielectric Liquids.—M. Berthelot.—The author has continued his experiments to liquids, taking care to control the strength of the current so as to prevent the formation of sparks in the liquid. He has tried turpentine, olive oil, and absolute alcohol. His results show that the discharge acts on organic liquids as on gases, causing polymerisations and the separation of hydrogen, but the action is much slower, because of the low conductivity and the great mobility of the liquids.

Action of Sulphate of Lime on some Alkaline Haloid Salts.—A. Ditte.—Not suitable for abstraction.

Preparation of Glucinum by Electrolysis.—P. Lebeau.—Will be inserted in full.

Chemical Estimation of the Carbonic Acid in the Air, even when only Present in Traces.—M. Nicloux.—The method used, which is described at length, makes it easy to estimate very accurately the amount of carbonic oxide present in the air, in proportions varying between 1/10000th and 1/50,000th.

The Dissociation of Carbides of Barium and Manganese.—MM. Gin and Leleux.—By using a very large current in the electric furnace, viz., 1600 ampères and 35 volts, the authors have succeeded in dissociating the carbides of barium and manganese and volatilising the metal, leaving a deposit of coke at the bottom of the crucible. In the case of the manganese, the characteristic reddish fumes due to the oxidation of the metallic vapour on contact with the air are easily observed.

Synthetic Isoborneols: their Identity with the Phenolic Alcohols.—G. Bouchardat and J. Lafont.—Not suitable for abstraction.

On the Partial Decomposition of Chloroform in an Organism.—A. Desgrez and M. Nicloux.—In some experiments with dogs the authors found that the quantity of carbonic acid in the blood increased in one case from 1·6 c.c. per litre to 2·9 c.c. after three hours ten minutes of anæsthesia: similar experiments on larger dogs showed even a greater difference. The authors therefore state that these experiments confirm certain conclusions already arrived at by them by means of their fire-damp meter—that chloroform is decomposed in the animal economy with formation of carbonic oxide.

Berichte der Deutschen Chemischen Gesellschaft.
1898, No. 2.

Decomposition of Wool Fat.—L. Darmsteadter and J. Lifschütz.—The fat was decomposed, after the wax had been separated, and an analysis made of the various acids and alcohols.

New Synthesis of Adenin and its Derivatives.—Emil Fischer.—Amido-oxychlorpurin is converted into adenin by the action of phosphorus oxychloride, which yields dichloradenin. This latter, on reduction with hydriodic acid, gives adenin. Methy-derivatives of adenin are similarly prepared from methylamido-oxychlorpurin.

A Fluosilicate and a Fluophosphate of Potassium and Rubidium.—R. F. Weinland and J. Alfa.—These salts are obtained by acting with HF on the sulphate and phosphate of potassium. Fluosulphate, $S_2O_7F_2HK_3.H_2O$, separates from a solution of neutral K_2SO_4 in a 40 per cent solution of HF in a crystalline form after concentrating by evaporation, and gives a good yield. The Rb salt is formed in the same way.

Formation and Change of Hylotropisomeric Substances.—Karl Schaum.

Separation of Mercury and Bismuth Salts.—L. Varino and F. Treubert.—A weak solution of mercuric chloride and bismuth oxychloride in HCl is decomposed with a mixture of hypophosphorous acid and hydrogen peroxide; the mercury is obtained quantitatively as calomel, whilst the bismuth remains in solution.

Molecular Weight of Solid Bodies.—J. Traube.—The author shows that the molecular co-volume of a solid is approximately half that determined for liquids in a previous paper. This proves an aggregation of molecules in pairs in the solid state. These results were proved experimentally for a large number of solid organic bodies. A similar property is shown also for many inorganic salts, which, as a rule, are bi-molecular aggregates. However, when in solution they give three ions; they are, for the most part, mono-molecular.

Some Thiourea Derivatives.—Rudolf Andreasch.—From thiourea the author prepared thiohydrantoin and a great many derivatives (ethyl thiohydantoin, ethylphenyl-thiohydantoin, &c.) as crystalline compounds. He was also successful in preparing from thiourea, thioparabamic acid, and parabamic acid. This reaction consisted in treating thiourea with cyanogen and subsequent hydrolysis.

Copper Compounds of Dicarboxylglutaconic Ester.—Wilhelm Wislicenus.—The author succeeded in preparing copper compounds of dicarboxylglutaconic ester by treating the latter with the calculated amount of copper acetate. Two such copper compounds were prepared; one neutral and one basic, which latter could be converted into the neutral by further treatment with dicarboxylglutaconic ester.

Condensation-products of Aldehyds with Phenol and Phenolcarboxylic Acids, and the Diphenylmethane Colour Derivatives of these.—Kahl Leopold.

Ammonium Peroxide.—P. Melikoff and L. Pissarjewsky.—If an ethereal solution of H_2O_2 is added to a large excess of an ethereal solution of ammonia, the substances being cooled with calcium chloride and snow, a solid compact crystalline substance is obtained. The crystals, after washing with cold ether, were dried on a tile and were analysed. They appeared to correspond to the formula $(NH_4)_2O_2+H_2O_2+H_2O$. At ordinary temperatures the substance decomposed, first dissociating into NH_3 and H_2O_2, and then giving off oxygen energetically, and forming a small quantity of ammonium nitrate.

Osmotic Pressure and Electrolytic Dissociation.—J. Traube.—The author determines the osmotic pressure of bodies in solution from a knowledge of the co-volume, which latter depends only on the concentration of the solution, and is independent of the nature of the dissolved substance.

Some Mono- and Di-halogen Ketones.—Franz Kunckell and Friedrich Johannssen.

Some Condensation-products of Piperonals, Vanillins, and Protocatechuic Aldehyds.—M. Rogon.

The so-called Nitramine and Isonitramine and their Ethers.—A. Hantzsch.—The author describes several nitramine and isonitramine compounds of the aromatic series, and shows the difference exhibited in their chemical and physical properties.

Diazo-compounds of *m*-Phenylendiamine.— K. Eiermann.—The compounds formed by this reaction are diacetyltriamidoazobenzene and triamidoazobenzene. The former was diazotised again, and after treatment with more phenylendiamine, yielded a diazo-product of the latter; this compound has been known as Bismarck brown, though its constitution has not hitherto been proved.

Addition of Cyanogen to Sodium Salt of Malonic Acid.—Wilhelm Traube.—An alcoholic solution of acid sodium malonic ether absorbs cyanogen when it is heated. The liquid becomes intensely red, and after a short time a dark red crystalline precipitate comes down. The analysis of this product shows it to have the composition—

$$HN{:}C.CNa(COOC_2H_5)_2$$
$$HN{:}\dot{C}.CNa(COOC_2H_5)_2$$

Some Brominated Ketones.—Franz Kunckell and Wilhelm Scheven.—A number of these substances were prepared from bromacetylbromide on phenol and its ether.

Homologues of Oxalacetic Esters. — Wilhelm Wislicenus and Max Kiesewelter.

Hydrazinacetic Acids. — Wilhelm Traube. — This substance, the amido-glycocoll, was obtained in crystalline form from oxybenzylhydrazinacetic acid on hydrolysis. The ethyl ester of this acid was prepared; also the ethyl ester of amidohydrantoinic acid and amidohydrantoin itself.

The Proteolytic Enzyme of the Saps of Yeast.— M. Hahm.

Separation of the two Desmotropic Forms of Acetoacetic Esters.—Robert Schiff.

Alcoholic Fermentations without Yeast.—Eduard Buchner and Rudolf Rapp.

Aliphatic Nitroso-compounds.—O. Piloty and O. Ruff.

MISCELLANEOUS.

Royal Institution of Great Britain.—The following arrangements have been made for the Friday Evening Lectures after Easter:—

April 22. W. H. M. Christie, C.B., M.A., F.R.S., Astronomer Royal, "The Recent Eclipse."

April 29. Professor Andrew Gray, M.A., LL.D., F.R.S., "Magneto-optic Rotation and its Explanation by a Gyrostatic Medium." (With Experimental Illustrations).

May 6. Edward A. Minchin, M.A., Fellow of Merton College, Oxford, "Living Crystals."

May 13. Professor W. A. Tilden, D.Sc., F.R.S., "Recent Experiments on certain of the Chemical Elements in relation to Heat."

May 20. The Right Hon. D. H. Madden, LL.D., "The Early Life and Work of Shakespeare."

May 27. Lieut.-General The Hon. Sir Andrew Clarke, R.E., G.C.M.G., "Sir Stamford Raffles and the Malay States."

June 3. Professor W. M. Flinders Petrie, D.C.L., "The Development of the Tomb in Egypt."

June 10. The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

Other Lectures will be delivered as follows, on the dates mentioned, at 3 o'clock precisely:—

Tuesdays, April 19, 26. Two Lectures on "Phases of Art—Past and Present," by Thomas Cooper Gotch.

Tuesdays, May 3, 10, 17, 24. Four Lectures on "The Historical Development of Europe," by Samuel Rawson Gardiner, M.A., D.C.L., LL.D.

Tuesdays, May 31, June 7. Two Lectures on "Literary Criticism in Greece," by Prof. S. H. Butcher, LL.D., Litt.D.

Thursdays, April 21, 28, May 5. Three Lectures on "Some Leaders in the Poetic Revival of 1760 to 1820—Cowper, Burns, and Scott," by the Rev. Canon Ainger, M.A., LL.D.

Thursdays, May 12, 19, 26. Three Lectures on "Natural Philosophy," by The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

Thursdays, June 2, 9. Two Lectures on "Modern Methods and their Achievements in Bacteriology," by Edward E. Klein, M.D., F.R.S.

Saturdays, April 23, 30, May 7, 14. Four Lectures on "Programme Music," by Sir Walter Parratt, Mus.Doc. (with Musical Illustrations).

Saturdays, May 21, 28. Two Lectures on "The Biology of Spring," by J. Arthur Thomson, M.A.

Saturdays, June 4, 11. Two Lectures on "The Temples and Ritual of Asklepios at Epidaurus and Athens," by Richard Caton, M.D., F.R.C.P. (with Lantern Illustrations).

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THE CHEMICAL NEWS.

VOL. LXXVII., No. 2003.

BAKERIAN LECTURE.

FURTHER EXPERIMENTS ON THE ACTION EXERTED BY CERTAIN METALS AND OTHER BODIES ON A PHOTOGRAPHIC PLATE.*

By W. J. RUSSELL, Ph.D., V.P.R.S.

IN a paper read before this Society in June last (*Roy. Soc. Proc.*, lxi., p. 424; CHEM. NEWS, lxxv., p. 302) it was stated that certain metals, alloys, and other substances,—such as picture copal, printing ink, straw board, &c.,—were able to act even at a distance on a sensitive photographic plate, producing effects similar in appearance and developed in the same way as plates which had been acted on by ordinary light. At that time sufficient experimental evidence had not been obtained to determine the nature of this action, or even to clearly indicate its general character, whether in fact the action rose from vapour given off by the active body, or whether phosphorescence was produced which acted on the plate. That bodies so slightly volatile as zinc, aluminium, nickel, &c., should be able to give off at ordinary temperatures in a few days sufficient vapour to act strongly on a photographic plate, and that such vapour should be able to pass rapidly through media, such as gelatin, celluloid, collodion, &c., seemed difficult to realise, although many of the earlier experiments appeared to indicate that this was the kind of action which took place. Later experiments confirm the view that a vapour is given off, which is the cause of the action on the plate.

Certain organic bodies, as well as metals, have been shown to act on the photographic plate, and in endeavouring to ascertain the nature of this action experiments with organic bodies were first undertaken, as the results which they yield are more easily and rapidly obtained than those with the metals, and if their mode of action was determined it would probably throw light on the action exerted by the metals. In the former communication it was stated that printing ink and copal varnish are active substances, both when in direct contact with a photographic plate and when at a distance from it. Further, it was found that the action which they exerted was able to pass through different media. Although printing inks and copal varnishes may vary considerably in composition, the main constituents are constant,—hence it was easy to determine that boiled oil and turpentine were the bodies to which they owed their activity, and that these bodies separately behaved in the same way as did printing ink and copal varnish. Boiled oil—that is, linseed oil which has been heated with oxide of lead—is an active substance, and most of the following experiments have been made with the pale drying oil which is prepared by Messrs. Winsor and Newton. Pure turpentine is also a very active substance, and, owing to its volatility, in many experiments very useful. These bodies can be used either as liquids in small dishes or by saturating Bristol board or other neutral and porous bodies, such as ignited pumice stone, &c., with them. In the case of the drying oil it can be painted on glass or cardboard and allowed to harden.

The experiments described in the former communication have been repeated under the same and under slightly different conditions and in another laboratory; the results obtained, with one exception, confirm the previous statements. Glass, selenite, mica, even in very thin layers, are absolutely opaque to the action, whereas gelatin, celluloid, collodion, gutta-percha, tissue tracing-paper, parchment, and paper are more or less transparent. Linseed oil and turpentine may fairly be taken as typical examples of active organic bodies. This property of acting on the photographic plate is far from belonging to all volatile organic bodies; for instance, although vegetable oils have the power of acting, mineral oils, so far as they have been tried, have not the power. Benzene, carbon disulphide, chloroform, &c., also are without this power of acting on the photographic plate; but the question of what substances are and what are not active will be dealt with on another occasion; at present it is simply to consider the conditions under which linseed oil and turpentine act on the photographic plate. The picture copal varnish which was much used in the former experiments obviously owes its activity to the turpentine and the oil it contains. Warm the varnish for some length of time; these bodies are driven off, and an inactive gum remains. This experiment obviously suggests a vapour as the cause of the action; at the same time such a vapour would pass through bodies such as gelatin, celluloid, &c. With regard, for instance, to the thin sheet gelatin, it appears to offer but very slight obstruction to the action of these organic bodies; if the thickness of the gelatin be increased still the action takes place, only the time of exposure has to be considerably longer.* Another striking fact with regard to this emanation from these active bodies is that it gives an accurate picture of the surface from which it has come. A hard copal surface on glass will give a picture showing every brush mark, unevenness, and scratch on the surface, and if the action take place through a thin sheet of gelatin, or even as many as six or more sheets, still the picture of the scratches is distinct. The following experiments are apparently strong evidence that the action on the photographic plate is due to the vapour given off from these organic bodies.

A piece of Bristol board saturated with drying oil, or a piece of glass painted with it or with picture copal, is placed on the bottom of an ordinary plate box, and a photographic plate larger than the active body is suspended above it with the film upwards; light is excluded from the box, and the arrangement is left for, say, a fortnight; then the plate when developed will be found to have been acted on irregularly round its edge, at some parts considerably more than at others, but everywhere shading off and evidently in the way, which would occur if a vapour had rolled round the edge. Another experiment which showed this kind of action very satisfactorily was carried out as follows:—A circular piece of the Bristol board was saturated with drying oil, and at a little distance above it a smaller circle of mica, which is perfectly opaque to the action, was placed, and again above this was another piece of mica with a circular hole smaller than the circular mica plate, and then the photographic plate was placed above. By this arrangement no direct action could take place between the drying oil and the sensitive plate, but a vapour could work its way between the mica plates, and thus reach the photographic plate; and this it did, for after an exposure of three days, on developing the plate there was a dark ring formed shading off towards the centre. Another and very simple experiment illustrating this same point is to place a small circular glass dish, with some drying oil in it, in the middle of a photographic plate, and leave it there for a week. On developing the plate it will be found that no action has taken place where the dish stood, but that immediately beyond the outside of the dish much action has occurred, and that the darkening gradually fades away. There is still another way in which the action of

* A Lecture delivered at the Royal Society, March 24th, 1898.

* The thin gelatin is 0·02 m.m. and the thick 0·16 m.m. in thickness.

these organic bodies has been tested, and that is by transferring the active power of these bodies to a neutral substance. If vapour be the immediate cause of the darkening of the photographic plate, then it would be possible, if a piece of Bristol board were suspended above drying oil, for instance, for the inactive board to take up those vapours and become photographically active. This was found to take place. Bristol board of good quality is a very useful substance in all these experiments, both as a screen and as an absorbent. It is in itself an inactive body, and may be heated in a water-bath before using, to prevent the accidental presence of any substance which might act on the plate. If a piece of the Bristol board be suspended above drying oil, in the liquid or solid state, or turpentine or picture copal for two or three days, or even less, it becomes strongly active, and when placed in contact with a photographic plate quickly darkens it. This action of the Bristol board is well shown, if a pattern be stamped upon it, which is easily done by pressing against it a piece of white net; black net must not be used, as it is slightly active; then the charged Bristol board will give an unmistakable picture. If turpentine be the active substance used to charge the Bristol board the exposure need only be for a few hours, but if after this charging it be exposed to the air for a day or two its activity will be found to have gone. There is obviously no visible indication of this activity of the Bristol board, and consequently if a device be cut out on a screen which is placed in front of a sheet of cardboard, or any inactive paper, and it is exposed to turpentine or to oil, or if the vapour of these bodies be in any other way brought in contact with the paper, a dark picture of such device, which is not visible, may be produced. Some unexpected and curious cases of ghostly pictures thus formed have been met with; they are, however, all produced in this way, and need not be described now. The above experiments have been made at ordinary temperatures, but if the temperature be increased the activity of these organic bodies is also greatly increased. High temperatures cannot, of course, be used, but a temperature of 55° C. does not appear to alter the photographic plate. With drying oil—which is one of the most active substances that has been used—it is easy to obtain a picture in thirty minutes at the above temperature. The interesting pictures which in the former communication it was shown could be produced simply by laying a piece of dry wood or the section of the branch of a tree on a plate are produced by the volatile matter contained in the wood. These pictures appear at first sight very accurate and complete; but this is not really so, for some parts of the structure of the wood is not shown and other parts are too strongly developed, depending on the amount of volatile substance present in the different parts. It is, however, very remarkable that so small a quantity of the volatile body as exists in a piece of dry wood should be able to produce a picture: the activity of the wood is increased by the presence of moisture. This property of acting on the photographic plate, possessed by the linseed oil, belongs apparently to the vapour and not to the oil itself; for if a sheet of thin gelatin be placed on a photographic plate, and on it a thick glass ring nearly filled with oil, and over the top of the ring another sheet of gelatin, not in contact with the oil, and another sensitive plate, it will be found that after a week's exposure no action has taken place below the oil, but that a large amount has occurred above it where the vapour has penetrated the upper sheet of gelatin. A similar result is also obtained by simply floating a piece of the thin gelatin on a dish of oil and placing a sensitive plate above. At the sides where the vapour can form and get away there is action on the plate; in the centre there is none.

In addition to glass, mica, and bodies of that kind, the action does not take place through a layer, except it be very thin, of either gum arabic or of paraffin. If a piece of Bristol board or a glass plate has hardened drying oil on it, and be painted over with a strong solution of gum arabic which is allowed to dry, then the delicate cracking which occurs can be very well shown on a photographic plate.

Pure water does not act on the plate, neither does pure alcohol or pure ether, but the ordinary commercial specimens of the last two bodies do, and often to a considerable extent. Alcohol which produces a dark picture will, after digestion with lime and careful distillation, be entirely inactive, and ether after careful purification also becomes inactive. Moisture, if present, does not effect this result; thus the presence of certain impurities, and they appear to be some of the most common ones, can be readily photographed, and approximately their amount determined by the darkness of the picture formed, so that by this means can be determined whether, for instance, a purification process is working well and whether it has completely done its work. The pictures are easily obtained by placing some of the liquid to be tested in a small glass dish, and a sensitive plate above it. Obviously it is only certain impurities which will be indicated in this way, but the reaction is otherwise of considerable importance, for it gives a simple method of determining what bodies soluble in these liquids are capable of acting on a sensitive plate. This matter will be treated of in a separate communication.

That the vapour given off by these organic bodies is the immediate cause of the action on the sensitive plate the above experiments seem to show. At the same time it is remarkable that such a vapour should readily pass through media such as gelatin, celluloid, &c., and not by mere absorption, but in such a way as to produce a picture of the surface from which it emanated.

Passing on to the action which certain metals exert on a photographic plate, results have been obtained which are strikingly similar to those just described. Substitute a piece of polished zinc for a piece of Bristol board saturated with linseed oil, and similar effects are produced on a photographic plate; the time of exposure must, however, be longer. Although both magnesium and cadmium are slightly more active than zinc, this last metal is the most convenient one to experiment with, and has been used in most of the following experiments. In addition to the above three metals, nickel, aluminium, lead, and bismuth have the same property, but not so strongly developed, of acting, both when in contact and when at a distance on a photographic plate. Cobalt, tin, and antimony can also act in the same way, but their action is considerably feebler, and undoubtedly other metals can act in the same way, but require much longer exposure. Mercury, which in the former paper was stated to be the most active of all the metals which had been tried, is now found to be quite inactive; the metal used in the former experiments was impure. This matter will be explained further on.

As so strong a similarity exists between the effects produced by the above-mentioned organic bodies and the metals, the question which naturally presents itself is, do they also give off a vapour which directly or indirectly acts on the photographic plate? The following experiments show that such an action does probably occur. Zinc which has been long exposed to the air is inactive. An exposure out of doors for only three or four days diminishes very considerably its activity, but covered up in doors after three weeks it will still give a tolerably dark picture. If it has a bright but perfectly smooth surface it is active, but not strongly so; rub the zinc with coarse sand or emery paper, and it is then obtained in its state of greatest activity; the same applies to all the metals. If, when in this condition, any of the active metals be placed in contact with a photographic plate, a beautifully sharp picture of the scratched surface is obtained. The great increase of the fresh metallic surface produced by the rubbing may account for the increase of activity which the scratching produces. If the zinc plate be raised only slightly above the photographic plate, a

sharp picture of the scratches is still obtained, and of course as the distance is increased, so is the indistinctness of the picture increased, and at last it fades into a general cloudiness, and in this form the zinc plate can easily be made to act through the distance of an inch or more.

This action of the metals passes through the same media as do the vapours from the organic bodies, and clear pictures can be obtained through sheets of thin gelatin, &c.; in fact, what has already been said with regard to the transmission of the activity of the organic bodies applies to the metals; gelatin, both thin and thick, allows the action of the metal to pass through it; celluloid and collodion do the same, and so does gold-beaters' skin and tracing paper. Reasoning, then, from this strong analogy between the action of the organic and the metallic bodies, it must be assumed that the above-mentioned metals from a clean surface and at ordinary temperatures give off vapour, and this vapour apparently acts when under the same circumstances in a like manner to the vapour given off by the drying oil. It gives a clear picture of the metal surface from which it arose, and it can permeate the same media as the organic vapours. The remarkably clear pictures of, for instance, a zinc surface, which can be produced through a sheet, or even several sheets, of the thin gelatin proves that the action is not one of mere absorption.

To gain further knowledge on this point and test the porosity of these different media, the power of hydrogen to diffuse through them was tried by cementing specimens of the different substances on glass tubes, which were filled with hydrogen and placed over water. The action is somewhat remarkable, but requires further confirmation. With the thin gelatin ordinary diffusion does not occur, and a hardly, if any, perceptible rise of the water in the tube occurs on starting the experiment; but on standing for some length of time—two or three days—the water begins to rise, and after a week or more it will stand at a height of four or more inches above the level in the vessel, and there it remains at least for a month or more. With the thick gelatin there is no evidence of any diffusion occurring. Celluloid acts much in the same way as the thin gelatin, a column of water gradually rises and remains there. The action of the gutta-percha tissue is to absorb the hydrogen; the diffusion tube completely fills up with water, and remains full without showing any tendency to fall for a couple of months, and then the experiment was stopped. With tracing paper diffusion occurs in the ordinary manner, and the same happened in the single experiment tried with gold-beaters' skin. That the rise of the water in the diffusion tubes is not owing to a mere absorption of the hydrogen by the gelatin or gutta-percha has been proved by placing a considerable quantity of these bodies in a tube sealed up at one end, filled with hydrogen and inverted over water; after several weeks no rise of the water in the tube occurred. The above experiments have been repeated with the same results, but further trials are being made. Possibly the metallic vapour is in a still finer molecular state than ordinary hydrogen, and thus is able easily to permeate a medium which hydrogen can only slowly get through, and air cannot get through. At all events, this may be looked upon for the moment as a working hypothesis.

That the action of the metals like that of the organic bodies is due to a vapour can be demonstrated by experiments exactly similar to those already described. For instance, if the thin mica plates be arranged above a zinc plate, in the way already mentioned, so as to cut off all direct action between the zinc and sensitive plate, a ring of action is produced which can only be accounted for by supposing a vapour present, which has worked its way between the sheets of mica and thus gained access to the photographic plate. Again, a piece of Bristol board can be made active by contact with, or mere proximity to, a piece of polished zinc. A striking instance of this arose in the following way:—A piece of perforated zinc had lain on the bottom of an ordinary plate box for a considerable length of time, probably about two months; the zinc was then taken away, and a sensitive plate dropped into its place. On developing this plate, a picture of the perforated zinc was obtained. Other experiments of a similar kind have been made. If the Bristol board be not in direct contact with the zinc; if a screen, with holes cut out in it, be interposed, it will be found that the Bristol board where exposed to the direct action of the zinc will become active, and will give an exact picture of the holes or whatever design it may be which has been cut out on the screen. To produce this effect the cardboard has to be exposed to the zinc for fully six weeks. This changing of the Bristol board does not take place satisfactorily above ordinary temperatures. With other metals than zinc, these changing effects have not as yet been obtained.

Another experiment, which illustrates the way in which the metals can act, is to take a piece of ordinary perforated zinc, polish one side, and lay this polished side against a plate of plain glass in a printing frame, then place the photographic plate against the dull side of the perforated zinc, and leave it in the dark for three or four days; then, on developing the plate, a reversed picture is obtained,—that is, the holes in the zinc will be represented by dark spaces, and the zinc itself by light ones. If the holes in the perforated zinc are large they are represented by shaded circles, so that these pictures are produced by the vapour emitted by the polished zinc which has crept into the open spaces and thus gained access to the photographic plate. It has already been shown that the action exerted by zinc passes more readily down a glass than down a paper tube of the same size: this has been strikingly confirmed by taking two pieces of glass tubing 1 inch long, $\frac{3}{4}$ inch in diameter; inside one a single coil of inactive paper was placed, and both tubes stood on a sheet of polished zinc, and a photographic plate rested on the top of them. They were then left for a week, and on developing the plate a black patch appeared above the tube without the paper, and no action was visible above the one with the paper. Without removing the paper, it was painted over with melted paraffin, and again a photographic plate put on the top of the two tubes; now two circular dark patches were produced of equal intensity.

If the activity of the zinc depends on a vapour which it emits, it seemed possible that it could be carried along by a stream of air. In order to try whether this was the case, a tube a foot long was packed with zinc turnings which had been amalgamated, and a stream of pure air sent through it. The end of the tube was fixed into the side of a dark box and a sensitive plate with a screen upon it suspended above it; thus no direct action could be exerted by the amalgamated zinc on the plate. The experiment was continued for four days, then, on developing the plate, a picture of the screen above where the tube entered the box was obtained, but at the other end of the plate there was no action.

The presence of mercury in this experiment was unsatisfactory, and might account for the result obtained, therefore an exactly similar experiment was made, and zinc turnings alone were used and a plate without a screen. The experiment was carried on for a week, and it was then found that a black patch had been produced immediately above the end of the tube. To be sure that this darkening did not arise from the action of the air, the whole of the zinc was removed from the tube and again the air sent through it for a week; the sensitive plate showed no signs of any action having taken place.

To try whether any accumulation of the vapour, and hence an increase of action, could be brought about by an increase of zinc surface, two small circular glass dishes were taken, about $1\frac{1}{4}$ inches in diameter and $\frac{1}{2}$ inch in depth; into one a single disc of bright zinc foil was placed, and in the other twenty similar discs, then on the top of both vessels a photographic plate was placed. The single disc was raised on a piece of glass, so both end

discs were at the same distance from the plate. The discs were a little smaller than the glass vessels, and, owing to their not being quite flat, there was a space between each one. In two experiments there was no marked difference between the density of the pictures produced, the single disc produced as much effect as the twenty. A more direct way for the passing off of the vapour was then made by cutting a circular hole § inch in diameter through the centre of all the zinc discs, and now a very black central spot was formed by the twenty zincs, and of course there was a white spot with the single disc, so that the vapour accumulated to a very considerable extent in this central space.

It has already been mentioned that the statement in the former paper that mercury was the most active of the metals is incorrect. The error arose from not suspecting that a trace of any impurity would affect the activity of the mercury, and, consequently, not taking special precautions to insure its perfect purity. On repeating the former experiments with another sample of mercury it was found that no action occurred, which seemed very remarkable; moisture was added, the temperature was increased, but still no action took place; the addition of a little zinc to the mercury was then tried, and it was found that this made the mercury excessively active. The presence of a very small quantity of zinc is able to effect this change, certainly less than 1/300th per cent. It is very remarkable that so small an amount of the metal can cause so strong an action on the photographic plate, for the exposure to the vapour given off by such an amalgam need not, even at ordinary temperature, be longer than two to three days. If other active metals are dissolved in pure mercury they act in the same way; at all events, this applies to magnesium and to lead. If silver, on the contrary, be added it does not render mercury active, nor does sodium. This action of mercury, which contains zinc or lead, the most common impurities, is so readily recognised that it becomes a valuable test for its purity, and a very interesting means of following the effect produced by any purifying process. A specimen of mercury containing not more than 1/300th per cent of zinc gave a very dark picture; this mercury was then treated first with sulphuric acid and afterwards, for three days, with nitric acid, and the picture it then gave was very faint, and on repeating this purifying process no picture at all was produced. Again, a sample of mercury containing zinc was carefully distilled. The distillate gave a very faint but very distinct picture. Another sample of distilled mercury also gave a faint picture.

Temperature, as might be expected, affects greatly this activity of the metals; at 4° or 5° C. zinc has but little action on a photographic plate. Most of the foregoing experiments have been made at about 17° or 18° C., and some, as specially noted, at 55° C. The Ilford special rapid plates have been used.

It appears, then, from the above experiments that certain metals have the property of giving off, even at ordinary temperatures, vapour which affects a sensitive photographic plate, that this vapour can be carried along by a current of air, and that it has the power of passing through thin sheets of such bodies as gelatin, celluloid, collodion, &c.; in fact, so transparent are these bodies to the vapour that, even after it has passed through them, it is able to produce clear pictures of the surface of the metal from which it came. That much remains to discover with regard to this action of the metals is obvious, the most active metals are not the most volatile. Nickel is very active, cobalt only very slightly so, copper and iron are practically inactive. I hope before long to be able to bring before the Society further developments of these curious actions, both of metals and organic bodies.

The foregoing experiments have been made in the Davy-Faraday laboratory, and I beg to thank the managers of the Royal Institution for having allowed me to work in their laboratory. My thanks are also due to my assistant, Mr. Block, for the very careful and intelligent way in which he has aided me with the experiments.

March 24, 1898.—Additional experiments have been made with active organic substances, in order to determine to what class of bodies they belong. As already stated, linseed oil and turpentine were the two substances first found to be very active organic bodies, and following out these results it has been proved that vegetable oils in general have more or less this property of acting on a photographic plate. Linseed oil, for instance, is very active, olive oil only very slightly so. Even samples of "pure" linseed oil obtained from the different artists' colourmen vary considerably in the amount of action which they exert. The boiled, or drying linseed oil, has, at ordinary temperatures, the same activity as the ordinary oil, but under other conditions it appears there is some difference in their action. Another class of bodies, also called oils, namely the essential oils, have been found to be very active substances. Samples of commercial specimens of the following essential oils have been tried: —Peppermint, lemons, pine, juniper, bergamot, winter green, lavender, cloves, eucalyptus, cadjeput, and cedrat, and were all found to be active, and not only when used by themselves, but also when dissolved in a large amount of pure alcohol. It is well known that the active substances in the essential oils are bodies known as terpenes, and I have to thank Dr. Tilden for supplying me with pure specimens of these bodies; they are all of them remarkably active. Paraldehyde and benzaldehyde are also very active bodies. Ordinary aldehyde and formaldehyde, as they have been at present applied, are only slightly active. Guiacum, both when in powder and in alcoholic solution, is active, and so are powdered cinnamon, sweet spirits of nitre, and eau de cologne. Brandy is slightly so. Now the important property belonging to all these bodies is their reducing or oxygen-absorbing power, hence the conclusion that it is this property which enables them to act on the photographic plate. The mineral oils, purified petroleum spirit, alcohol, ether, the esters, such as ethyl acetate, benzene, nitrobenzene, are all, when pure, unable to produce any effect on a sensitive plate, and even oxidised bodies nearly related to the terpenes, such as terpinol and camphor, are not active, neither is thymol. Terebene is an exceedingly active body. The difference of activity of the ordinary oils seems to follow their oxygen-absorbing power, at all events it is so with regard to linseed and olive oils, for the former is the most active of the oils, and 1 grm. of it is said to be capable of absorbing 186 c.c. of oxygen, while the same weight of olive oil can absorb only 8·2 c.c. It is also interesting to note that at least with some of these active bodies results can be obtained which correspond to what photographers term solarisation or reversal, the action, when modified, giving a black picture, when carried to its full extent a white one.

It has already been stated that a mere trace of zinc makes mercury active, but it is certainly equally curious and unexpected that a trace of zinc should make alcohol active. It is only necessary to take pure alcohol and place in it some strips of bright zinc foil, leaving the metal in for three or four days. It will then be found that the alcohol can act strongly on a photographic plate. The same happens with ether and with ethylacetate, but not with benzene. In addition to zinc, cadmium, magnesium, aluminium, and fusible metal can act in the same way, whereas lead, nickel, tin, silver, sodium, and, as far as experiments have gone, all the inactive metals, have no such power. This reaction is still being investigated, but certain it is that careful filtration does not remove this activity from alcohol, nor does distillation entirely destroy it.

ON THE

COMPOSITION OF THE ATLANTIC OCEAN.

By C. J. S. MAKIN, F.I.C., F.C.S.

(Concluded from p. 156).

Potash.

This oxide is undoubtedly the most difficult to determine with accuracy. The conventional method of separation and weighing as K_2PtCl_6 was proved impracticable in such an enormous excess of soda. The present estimations were carried out in accordance first with the *Challenger* method and then with two modifications. One of the latter has been adopted. In the first, the sulphates obtained in the Na_2SO_4 estimation were dissolved in a little water and then rather more than 1½ parts of $PtCl_4$ added for every part of K_2SO_4 present. The mixture was evaporated short of dryness, and, on cooling, a fair quantity of a mixture of 2 parts of absolute alcohol and 1 part of ether added, and the mixture left for several hours. The precipitate was washed by decantation with a similar mixture of alcohol and ether, and then removed to a small filter and the washing proceeded with until the wash-water is quite colourless and a few c.c. of it are free from solid matter on evaporation. The precipitate is dried and reduced in a porcelain basin by a stream of hydrogen; heat up to 300° being employed. The residue is washed with water and dilute hydrochloric acid, and the platinum finally weighed. This weight multiplied by 0·4747 equals K_2O in sample taken. In the *Challenger* estimations, the proportions of potash were fairly constant, and it was found that 100 c.c. of water usually yielded about 100 m.grms. of platinum.

The Second Method.

Twenty-five c.c. of the original sea-water were rendered faintly acid and mixed with $PtCl_4$ in sufficient excess, and evaporated to a syrup without previous elimination of sulphuric acid. When cooled, 90 per cent alcohol was added, and, after the mixture had stood some hours, a little ether was poured into the basin. The precipitate, collected on a small filter, was washed until the filtrate was quite colourless, dissolved in boiling water, and poured in this condition into a boiling solution of formate of soda. The boiling was gently prolonged for five minutes, the precipitated platinum filtered off and weighed, and the same factor used as in the first estimations.

The Third Method.

The alkaline chlorides were carefully isolated from 25 c.c. of the sea-water and treated as in the last stage. The first precipitate of K_2PtCl_6 obtained was, however, dissolved in a very little boiling water, and the solution evaporated a second time with the addition of a little more $PtCl_4$. Subsequent treatment was similar to the last method.

The results were rather conflicting.

The first gave	103·70	m.grms. platinum
	103·61	,, ,,
The second gave ..	97·67	,, ,,
	98·04	,, ,,
The third gave	105·20	,, ,,
	105·26	,, ,,

The mean of the third was adopted. This figure (105·23(yields of K_2O 0·049952, or 0·07915 KCl.

Ammonia.

These determinations were made as follows:—100 c.c. of the sample and 400 c.c. of re-distilled ammonia-free water were distilled and nesslerised in the conventional manner. The bulk of the residual liquid was restored to 500 c.c. and excess of potash added. Distillation was then continued, and the ammonia estimated and returned as "ammoniacal salts." Permanganate of potash was then added, the volume restored to 500 c.c., and distillation proceeded with; this yields albumenoid ammonia. Finally, "moist combustion" was effected on 250 c.c. of the water, together with 500 c.c. of distilled water; the solutions employed and other details being in accord with Wanklyn's procedure. The estimations were made in triplicate. A small correction is made for the traces of organic matter in the half litre of distilled water. The results were in m.grms. per litre.

Free ammonia	0·188	0·194	0·192
Ammoniacal salts (NH_3)	0·359	0·364	0·362
Albumenoid	0·560	0·552	0·558
Organic matter in m.grms. of oxygen per litre	10·40	11·00	

There is every probability that the free ammonia found is far above the truth. The estimations were not made for some three months after the samples had been in the laboratory.

Composition of 1000 grms. of the general sample as compared with a published analysis of the English Channel.

	Sample.	Channel.*
Sodium chloride	28·023	27·059
Potassium chloride	0·770	0·766
Magnesium chloride	3·672	3·666
Magnesium sulphate	2·399	2·296
Calcium sulphate	1·365	1·406
Magnesium bromide	0·075	0·029
Calcium carbonate	0·129	0·033
	36·433	35·255
Water	963·567	964·745
	1000·000	1000·000

* Newth's "Inorganic Chemistry."

Comparison of Results between the present enquiry and the *Challenger* and Forchammer figures (surface water) to 100 parts of halogen.

	Challenger.	Forchammer.	Makin.
SO_3	11·576	11·88	11·908
Lime	3·053	2·93	3·154
Magnesia ..	11·212	11·03	11·721
Potash	2·405	1·93	2·410
Soda	74·760	Not determnd.	73·664

Comparison of Results calculated to 100 parts of total salts.

	Challenger.	Makin.
Chlorine	55·292	55·185
Deduct O for Cl_2 and Br_2..	12·493	12·454
	42·799	42·731
SO_3	6·410	6·593
CO_2	0·152	0·156
CaO	1·676	1·741
MgO	6·209	6·484
K_2O	1·332	1·334
Na_2O	41·234	40·783
Bromine	0·1884	0·1792
	100·0004	100·0012

By readjustment of the acid radicles with the oxides a further comparison may be made with the *Challenger* results, when the components are calculated to 100 parts of sea-water salts.

	Challenger.	Makin.
NaCl..	57·758	76·915
$MgCl_2$	10·878	11·407
$MgSO_4$	4·323	4·483
$CaSO_4$	4·070	4·226
K_2SO_4	2·465	2·468
$MgBr_2$	0·217	0·206
$MgCo_3$	0·290	0·298
	100·001	100·003

This comparison shows perhaps more thoroughly the true variation between the waters of the North and South Atlantic and the mean results of the *Challenger's* investigations, extending as they did over nearly every quarter of the globe.

ON THE PREPARATION OF GLUCINUM BY ELECTROLYSIS.

By P. LEBEAU.

In the year 1828 Bussy and Wöhler isolated glucinum, almost simultaneously, by acting on its chloride with potassium. Since this time the separation of this metal has been the object of numerous trials, but in spite of all it remains even now a delicate laboratory experiment. We will recall specially Debray's researches on this subject. The very dissimilar physical and chemical properties attributed to glucinum by the different *savants* who have prepared it, have led us to try and find a process by which it can be obtained in a state always comparable with itself and of a constant purity.

The reaction generally employed in preparing glucinum consists in making an alkaline metal, potassium or sodium, react on the chloride of glucinum (Bussy, Wöhler, Debray, Nilson and Peterson, Reynold, Humpidge), or on the double fluoride of glucinum and potassium (Kruss and Morath).—*Liebig's Annalen der Chemie*, cclx., p. 187. A few attempts have been made to obtain the metal by means of electrolysis; MM. Nilson and Peterson (*Ann. de Chim. et de Phys.*, Series 5, xiv., p. 426) were not able to decompose the chloride, and found that its electrical resistance was so high that the current could not pass through it. M. Borchers (*Zeit. für Electrochemie*, 1895) claimed to have obtained glucinum by decomposing the triple chloride of glucinum, potassium, and ammonium, by a current of 1000 ampères per square metre of electrode and 5 volts, but he did not describe the metal obtained. Finally, Mr. Warren (CHEM. NEWS, lxxii., p. 310) claims to have made glucinum on a commercial scale, by electrolysing bromide of glucinum, by means of a current of 8 ampères and 12 volts. The metal obtained, converted into *objets d'art*, are at the present time in the possession of the Amir of Afghanistan. The bromide of glucinum used by Mr. Warren was apparently impure, for we have found that the melted halogen salts of glucinum do not conduct the electric current.

The glucinum compounds formed by chlorine, bromine, and iodine are rather difficult to obtain, and their rapid alteration in the presence of water causes them to be of very little practical use. We thought that perhaps the fluoride of glucinum, the properties of which are so little known, might present some advantages. We succeeded in preparing this body in a state of purity; it melts very easily, giving a fluid of great transparency, but unfortunately it is an absolute non-conductor of electricity. However, the addition of fluoride of sodium or potassium makes it a conductor, and then the glucinum can be separated by electrolysis.

Marignac (*Ann. de Chim. et de Phys.*, Series 4, xxx., p. 45) has studied the double fluorides, formed by fluoride of glucinum and the alkaline metals, from the crystallographical point of view, and he has obtained compounds of the forms $GF_2,2MF$, and GF_2MF. Notably the salts of sodium, $GF,2NaF$ and GF,NaF, which agree perfectly; the first melts at about 350°, giving, on cooling, a transparent vitreous mass; the second, which melts at a dull red heat, gives, on the contrary, a white mass with a crystalline fracture. This latter salt, having the lowest electrical resistance, would be chosen by preference when we have not a very strong current at our disposal.

We can prepare these salts by Marignac's method, which consists of mixing the concentrated solutions of the fluorides, and allowing them to crystallise; or we can dissolve the pure hydrate of glucinum, and carbonate of sodium in the exact calculated proportions, in hydrofluoric acid. The liquid is evaporated to dryness, and the residue melted in a platinum crucible. This double salt may then be poured on to a sheet of platinum to cool, and kept in a stoppered glass bottle. If the quantity of fluoride of glucinum present is lower than that which corresponds to the formula GF_2NaF the product will become deliquescent.

The electrolysis is carried on very conveniently in a nickel crucible, which serves as the negative pole, the positive electrode consisting of a sheet or rod of graphitic carbon, which will not disintegrate under the influence of the current. We begin by melting the salt by means of a Bunsen burner; we then pass the current and withdraw the heat. The mass remains in fusion; too great a temperature is not needed, and it should not exceed a very dull red.

We had at our disposition the current produced by a small dynamo designed for charging accumulators, giving a normal current of 20 ampères and 80 volts. The current we used during the experiment was from 6 to 7 ampères, and from 35 to 40 volts.

After about 45 minutes, and using a crucible capable of containing 100 grms. of the salt $GF_2,2NaF$, we obtained on the nickel crucible—above all in the median part—a metallic deposit formed of a non-adherent, felted, crystalline mass, which we isolated and treated with boiling water. After prolonged washings the disaggregation was complete, and we collected a powder formed entirely of rather irregular crystals, such as is often met with in electrolytic deposits, and which consists of pure glucinum entirely free from nickel and iron. Under the microscope it has a brilliant white metallic appearance; it does not contain any trace of amorphous matter.

We have, further, been able in these experiments to obtain alloys of glucinum, by working in carbon crucibles which served as the negative pole, and also contained the metal to form the alloy in a state of fusion: it is thus that we found it possible to prepare over again the glucinum bronzes, the preparation of which, by means of the electric furnace, we have previously described.—*Comptes Rendus*, cxxvi., No. 10.

NOTE ON THE SEPARATION AND ESTIMATION OF LEAD, COPPER, AND ARSENIC.

By F. JEAN.

This method consists in precipitating the hydrochloric solution, containing lead, copper, and arsenic, by a current of sulphuretted hydrogen, so as to separate these metals in the state of sulphides from the other bodies precipitable by sulphide of ammonium.

The precipitate of the mixed sulphides thus obtained is washed by decantation, then digested warm with a few drops of concentrated Javel water to oxidise the sulphides. When the solution is decolourised it is acidulated with a few drops of sulphuric acid and boiled to drive off the excess of chlorine. It is allowed to cool, and alcohol is added to render the sulphate of lead insoluble; filter, and from the weight of sulphate of lead found the percentage of lead present is calculated.

The filtrate, now free from lead, is warmed to drive off the alcohol; we then add ammonia in sufficient quantity to re-dissolve the precipitated arseniate of copper which forms at the commencement of the neutralisation.

The copper contained in this ammoniacal solution is titrated by means of a solution of sulphide of sodium. The final point of the titration is observed by placing one drop of an alkaline solution of lead on a white filter-paper by the side of a drop of the solution to be tested; the

moment the precipitation of the sulphide of copper is complete a brown arc is formed at the point where the two moist spots touch.

The titration of the copper being finished the solution is made acid by means of dilute hydrochloric acid, and the sulphide of copper is separated by filtration. It is necessary to acidulate before filtration, so as to be sure of separating a small quantity of sulphide of copper which is soluble in the alkaline solution. To the filtrate, containing arsenic acid, are added a few crystals of chlorate of potash; it is then concentrated by boiling to about 20 c.c.; we then nearly neutralise with ammonia, and add 5 c.c. of acetate of soda, and titrate the arsenic acid by means of an acid solution of acetate of uranium, observing the same conditions as when titrating phosphoric acid by Joulie's method.

The above method, applied to the analysis of the mixture, gave the following results:—

	Contained.	Found.
Lead	0·122 grm.	0·1212 grm.
Copper	0·020 ,,	0·020 ,,
Arsenic	0·0375 ,,	0·0370 ,,

—*Journ. de Pharm. et de Chimie*, vii., No. 5.

A SIMPLE AND ACCURATE METHOD OF TESTING DIASTATIC SUBSTANCES.

By JOKICHI TAKAMINE.

There are various methods known for determining the diastatic power of substances, as Lintner's, Junk's, and others. While some of these are very reliable in many respects they are complicated, and require specially trained hands to get reliable results. They are not, therefore, applicable when quick, simple, and accurate testing is desired, as in diagnosing a certain form of amylolitic dyspepsia by determining the diastatic power of the patient's saliva. My proposed test method is based upon the stable diastatic property of Taka-diastase.

So far as is generally known, and it is also my own experience, the diastase isolated from malt, and that precipitated principle of saliva known as ptyaline, lose their diastatic power by standing. Therefore, when the diastatic power of any substance is to be determined, it is necessary, if they are used, to go through the long process each time of determining the quantity of sugars formed by their action on starch (Lintner's method), or else measure the length of time required to convert the given quantity of starch into sugar (Junk's method). While these processes have valuable merits of their own, yet they have the disadvantage of being rather complicated for quick every-day work. In carrying out my proposed method, a quantity of Taka-diastase is tested by either of the above-mentioned processes (Lintner's or Junk's*), and its exact diastatic power determined once for all. The diastatic power may be expressed as, say, 300 Lintner's units, or it may be expressed as converting 100 times its own weight of dry starch into sugar in ten minutes.

The diastatic power of any substance under examination is now compared with the standardised sample, and expressed in any terms desired, either directly, or by simple calculation. It is highly desirable that one standard should be adopted, and, whatever that may be, the following comparative test will be found useful. First prepare the following solutions:—

1. *Standard Taka-diastase Solution.*—Dissolve 1 grm. of standardised Taka-diastase solution in 100 c.c. of water; this solution ought to be made fresh each day.

2. *Starch Solution.*—Make a 5 per cent solution of neutral potato starch by boiling 800 c.c. of distilled water in a suitable wide mouth vessel; pour into it milk of starch, made by stirring 50 grms. of starch into 200 c.c. of cold water, and boil two minutes.

3. *Iodine Solution.*—Place 1 grm. of iodine and 2 grms. of potassium iodide in a flask, add a little water, say 5 c.c., agitate until dissolved, and dilute to 120 c.c.; or dilute 50 c.c. tincture of iodine, U.S.P., with 50 c.c. of water containing 2·5 grms. of potassium iodide.

Apparatus Required.—(1) One quart agate-ware kettle; (2) one shallow tin pan, 2 inches deep, 8 inches in diameter; (3) two 1 c.c. pipettes graduated to tenths; (4) eight large glasses or tumblers of about 150 c.c. capacity each; (5) ten small test-tubes; (6) one 100 c.c. cylinder; (7) two white dinner plates.

Process of Testing.—Pour into each of the eight glasses 100 c.c. of the hot starch paste. Place them side by side in the shallow pan of warm water at about 40° C. Measure into the first glass 1 c.c. of the saliva or other liquid to be tested. Pour, of the standard diastase solution, in quick succession—

Into the second glass	.. ..	1 c.c.
,, third ,,	.. ..	2 ,,
,, fourth ,,	.. ..	3 ,,
,, fifth ,,	.. ..	4 ,,
,, sixth ,,	.. ..	5 ,,
,, seventh ,,	.. ..	6 ,,
,, eighth ,,	.. ..	7 ,,

Then the contents of each glass is stirred with the test-tube as a stirring rod in quick succession, until the starch paste all becomes limpid. At this stage it will be observed that the stronger the diastatic power the quicker the liquefaction of the paste. When the contents of the glasses become liquefied, take out of each glass in succession a drop of the liquid by means of the stirring test-tube, and drop on a white dry dinner plate in the order of the glasses. When there are eight drops of equal size on the plate, drop on each one drop of the iodine solution. Then spread each sample with the finger to about the size of a silver dollar. The drops from the second to the eighth glass will form a colorimetric scale from blue to purple and reddish brown. Observe now which member of the scale corresponds to the colour of the one containing the saliva. The comparison is made more certain by repeating the tests within the first ten minutes after the saliva is put in.

Suppose the colour corresponds to somewhere between the fourth and fifth, then we can assume it at 4·5, and calculate the diastatic strength in terms of starch converted or sugar formed; or, if further accuracy of the test is desired, a scale of starch glasses containing standard diastase solution of 4 c.c., 4·2 c.c., 4·4 c.c., 4·6 c.c., 4·8 c.c., and 5 c.c., may be put up and compared with 1 c.c. of the given saliva in the same manner.

Instead of having only one specimen at a time, several samples of saliva or other diastatic substances can be tested at once.—*American Journal of Pharmacy*, vol. lxx., No. 3.

* Lintner, *Journ. für Prakt. Chem.*, [2], xxxiv., 378—394. Junk, *Am. Journ. Pharm.*, lv., 289, and lvii., 13; modified in *Bulletin of Pharmacy*, February, 1898, p. 52.

THE DIGNITY OF ANALYTICAL WORK.*

By C. B. DUDLEY.

It will doubtless be conceded by all, that in the choice of the field to which one proposes to devote his life-work, a number of things should be consulted. Among these may be mentioned not only mental capacity and the opportunities for training by courses of study, which may be available to him, but also what may be termed natural inclination or love for the work. Just how much weight should be given to each of these elements is a query not easily answered, but few will deny that genuine interest

* Presidential Address delivered at the Washington Meeting of the American Chemical Society, December 29, 1897. From the *Journal of the American Chemical Society*, vol. xx., No. 2.

in or real love for the field of work chosen, should be allowed as great sway as possible. Those of us who have gotten far enough along in our life-work to be able to look back somewhat, and to see and differentiate the causes that have shaped our line of effort, know full well that circumstances beyond our control, rather than our inclinations and desires, have in many cases determined our course, but the fact nevertheless remains, that for the best results, for the attainment of even moderate success, one's efforts must be in a field agreeable to him, and his heart must be in his work. Fortunate is the man for whom circumstances so shape themselves, that he is able to pass his years in the field of his choice, and spend and be spent in work that is congenial to him.

Assuming now that for most of us, circumstances and conditions have been such that we are spending our lives in the field of our choice, let us consider for a moment a tendency that seems to be a concomitant of those thus fortunately situated. Do we not occasionally find in ourselves a disposition to magnify the importance of the field in which we happen to be engaged? Are we not somewhat inclined, quite naturally perhaps, to think that our field of work is more important than that in which others are occupied? Does not the theoretical chemist, whose inclinations lead him to spend his time in writing reactions, and building structural formulæ of wondrous architecture, often feel within himself that his work is on a higher and nobler plane than that of the patient analyst, who has furnished the data which he uses? Does not the organic chemist who delights in the study of the carbon compounds, who can repeat for you series after series of chemical bodies, differing from each other by the constant addition of an element or group of elements, in whose vocabulary "types," "substitutions," "replacements," "condensations," and "isomers" are familiar words, and who, when a new organic compound is discovered, cannot rest until he has found to what series, and what place in the series, it belongs, or what its relations are to other bodies in that marvellous structure, based on the element carbon, which the studies of the last half century have reared before our eyes, I say does not this organic chemist oftentimes feel that he is engaged in a field far more worthy of study, and to which is due much more consideration than to that of his inorganic brother, who devotes days and perhaps weeks to unravelling the constitution of some obstinate silicate, whose crystalline form gives little help, and whose oxygen ratio is hidden or obscure? Or again, does not the physical chemist oftentimes think, that with the tools of his more especial field, with his specific heats, his vapour-densities, his heats of chemical combination, and his ions, he is quite competent to solve all problems worth solving in the realm of chemistry, and that those who are engaged in other lines are far below his standard, and can be looked down upon quite with pitying sympathy? Still once more, do we not often see the pure chemist whose battle cry is "original work for the work's own sake," claim for himself the highest seat in the synagogue, and refuse to join his efforts with those of others whom he regards as his humbler brethren, viz., those working in the field of applied chemistry, in securing the benefits of organisation to extend and widen the borders of our science? Finally, not to make distinctions, do we not frequently see the analyst who knows so well how necessary it is to have the trained and skilful hand, and the acute and watchful brain, both working together, and at the same time, in order to secure the accuracy, without which his work is worthless, claiming for his field, that it is the foundation upon which our science rests, and that those who spend their time in locating the position of an atom in its molecule, or in finding the relations of an organic compound to other members of its series, or perchance in inventing long names for new compounds in which all the resources of the ancient Greek and Latin are brought to bear, to reveal in one word the constitution of the compound, I say does not the analytical chemist often regard these workers as shallow, empty headed, and unworthy to be called chemists.

Now far be it from me to say that this partiality of each for his own field is blameworthy. We can, indeed, conceive of cases in which this partiality may be carried a little too far, but within proper limits, not only is it not blameworthy, but even as it seems to us, it may be praiseworthy for one to magnify the importance of the work in which he is engaged. A just and proper estimate of the value of his own work, a reasonable pride in his chosen science, or in that paddock of his science which it has fallen to the share of each to care for and cultivate, and indeed a moderate, though necessarily a somewhat partial, comparison of himself and his field of labour, with others, even though that comparison is somewhat to the detriment of the others, are not always necessarily bad. On the other hand, such pride and such comparisons tend to stimulate to renewed activity, tend to sustain in the perplexities and discouragements of work, and tend to keep one's effort concentrated on the work which he can do best. Looked at in this light, the generous rivalry of one branch of our science with another, or the pardonable pride of each in his own chosen field, and even in his own work, may be a distinct advantage, and I know you will bear with me a few minutes, while I, with proper modesty, and in the true sprit, I hope, try to magnify a little the field of analytical work.

To my mind, then, it is just and proper to take pride in analytical chemistry, because of the power which a properly conceived and executed analysis has of explaining difficulties. A few illustrations will, perhaps, make this point clear, and I am sure I will be pardoned for giving illustrations from my own experience, rather than historical ones.

Some years ago, after a passenger coach on the Pennsylvania Railroad had been through the hands of the car cleaners, it was noticed by some of the officers that the paint on the outside looked very badly, and had apparently been injured by the cleaning. A careful examination by the paint experts revealed the fact that the varnish was nearly all gone, and in some places the paint itself partially removed. As a matter of discipline, the car cleaners were called to account, and requested to explain why the paint and varnish had been so badly injured. Their reply was that with the soap that was furnished for car cleaning no better results could be obtained. This statement was, of course, received with a grain of allowance, it being well known to railroad operating officers, that almost universally when anything goes wrong, and the men are called to an account, the materials are blamed. However, in order to give the men the benefit of the doubt, a sample of the soap was obtained and submitted to analysis, when it was found that this soap actually contained over 3 per cent of free caustic soda and about 7 per cent of sodium carbonate. It is evident that this soap had been very carelessly made from cheap materials, and since it is well known that water solutions of both caustic and carbonated alkalies are fairly good solvents for dried linseed oil and other constituents of paint and varnish, it is clear that the defence of the men, in this case at least, was legitimate, and that the soap was really at fault. It may be added for information, that the circumstances above described led to the preparation of a specification for common soap, in which the amount of free and carbonated alkali was limited to very low figures, and that no similar difficulty of destruction of paint and varnish has since occurred.

(To be continued).

Osmotic Pressure and Cryoscopy.—A. Reychler.—This is a long mathematical paper in which the author criticises Mr. H. Crompton's deductions, that the law of van 't Hoff requires a correction, and he shows that the facts given by Mr. Crompton agree very well with van 't Hoff's law without any modification whatever.—*Bull. Soc. Chim. de Paris*, Series 3, vol. xix.-xx., No. 3.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, March 31st, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Mr. W. G. McMillan and Dr. Thorne were appointed scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's Address.

The President, in beginning his Address, remarked that the papers submitted to the Society during the past session included original work in all branches of chemical science. They have been contributed, not only from the laboratories of the older universities of Oxford and Cambridge, but also from the university colleges and other institutions throughout the country. The publications of the Society are, therefore, a complete record of English chemical Science, and of the researches pursued at different educational centres throughout the country.

The *Proceedings* are now the medium of publication, not only of abstracts of papers which will subsequently appear in the *Transactions*, but also of the rapid publication of short papers and preliminary notices.

The rule, which came into force last year, requiring that authors shall deposit their papers and abstracts with the Secretaries before they are officially announced for reading at a meeting, has worked well; it has made it possible to expedite the publication of the *Proceedings*, and to send advance proofs to the authors for correction.

The meetings have been well attended, the meeting-room being often quite full. Occasionally, interesting discussions have taken place, but as so many of our papers deal with details and matters of fact, anything like a debate must necessarily be of rare occurrence.

The following Past-Presidents, Lord Playfair, Dr. A. W. Williamson, Sir E. Frankland, Dr. W. Odling, Sir F. A. Abel, Dr. J. H. Gladstone, Sir J. H. Gilbert, this year complete a connection of fifty years with the Society. To mark its sense of the great services they have rendered to chemical science, the Council have resolved to entertain them, in the name of the Society, at a dinner on June 9th, given to commemorate their half century of Fellowship of the Society.

During the past year the Council has had under consideration the question of a revision of the Bye-laws. A Committee was appointed early in the year, which has met several times during the session, but, in view of the wider questions which have occupied the attention of the Council, they have not been able to complete their report.

During the session a section of the Fellows residing at a distance from London have expressed a desire to take part in the election of Officers and Council without being forced to undertake a journey to London to register their votes at the Annual General Meeting. A Memorial was drawn up, asking the Council to prepare and lay before the Society a Bye-law enabling Fellows to record their votes by post. This Memorial was signed by 540 Fellows, of whom 400 resided outside the London district. In the meantime, the By-law Committee had taken steps to ascertain the powers of the Society in this matter under their Charter. They were legally advised that any Bye-law framed to admit voting by post or proxy would be repugnant to the Charter, and therefore invalid.

When the Memorial was presented to the Council, a covering letter contained another suggestion, viz., that it might probably be necessary to obtain a Supplemental Charter, in order to enable the Council to carry out the wishes of the Memorialists. This suggestion was seriously considered by the Council, and further legal opinion was taken on the subject. They were advised that no application for a Supplemental Charter which was not supported by the practically unanimous wish of the Fellows would be listened to by the Privy Council. They have since been further advised that it would be *ultra vires* on their part to expend any part of the funds of the Society in applying for a Supplemental Charter. All the documents relating to the Memorial and the various legal opinions, together with the decisions of the Council, have already appeared in the *Proc. Chem. Soc.*, 1898, pp. 1, 33, 61.

The following eminent foreign chemists, whose names are familiar to us all as of those who have advanced knowledge in various departments of our science, were elected Foreign Members in January of this year, bringing the total number of Foreign Members of the Society up to 38:—Professors S. Arrhenius, Th. Curtius, A. P. N. Franchimont, W. Körner, W. Markownikoff, N. A. Menschutkin, H. Moissan, W. Ostwald, F. M. Raoult, I. Remsen, W. Spring, L. J. Troost, P. Waage, J. D. van der Waals. The Society has lost a Foreign Member by death: Professor Victor Meyer, one of the most brilliant and original of the modern school of chemists. The Kekulé Memorial Lecture has been delivered by Professor Japp. It has been resolved that the Memorial Lectures delivered up to 1896 shall be bound and published as Vol. I. of the Society's Memorial Lectures as soon as possible.

The Council have nominated the Treasurer and Editor as Delegates for the Society to the National Committee appointed by the Royal Society to prepare a Catalogue of Scientific Literature.

The remainder of the President's Address was devoted to an account of recent advances in Low Temperature Research, which will subsequently appear in the *Transactions*.

The numerical strength of the Society was as follows:—

Number of Fellows, March 31st, 1897		2079
since elected		114
reinstated by Council		4
		2197
Removed on account of non-payment of two annual subscriptions	17	
Withdrawn	22	
Deaths	18	
	—	57
Number of Fellows, March 31st, 1898		2140
Foreign Members		38

Fourteen Foreign Members were elected during the year.

The following have died:—J. J. Bowrey, G. W. Child, E. H. Gaskell, B. H. Gibbins, W. A. L. Hammersley, S. J. Harris; Walter Jardine, G. A. Keyworth, M. H. Lackersteen, Samuel Lees, Herman Lescher, Thomas Mitchell, Howard Newton, F. M. Rimmington, J. W. Rodger, Taraprasanna Roy, W. J. Saint, James Napier.

The number of communications made to the Society during the year was 127.

One hundred and fourteen papers were published in the *Transactions* for 1897, occupying 1204 pages, whereas in the preceding year 117 papers were published, occupying 1702 pages.

The following were the statistics relating to the Abstracts. (See next column).

Eight hundred and fifty volumes had been borrowed from the Library. The additions comprised 78 books, 282 volumes of periodicals, and 36 pamphlets.

Sir W. Crookes, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*.

Dr. W. J. Russell, F.R.S., seconded the motion, which was carried by acclamation.

The President having returned thanks,

Dr. Thorpe, F.R.S., the treasurer, gave an account of

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	648	1049
PART II.		
General and Physical Chemistry		324
Inorganic Chemistry		270
Mineralogical Chemistry		192
Physiological Chemistry		168
Chemistry of Vegetable Physiology and Agriculture		158
Analytical Chemistry		414
Total in Parts I. and II. ..	612	1526
	1260	2575

the balance sheet, which he laid before the Society, duly audited.

The receipts had been:—By admission fees and subscriptions, £3827; by sale of Journal and advertisements, £686 3s. 6d.; and by dividends on invested capital, £414 6s. 0d. The expenses had been:—On account of the Journal, £2963 11s. 1d.; on account of the Proceedings, £278 7s. 10d.; on account of the General Index, £182 18s. 1d.; on account of the Library, £307 4s. 9d.; House expenses, £203 6s. 7d.; the total expenditure being £4807 6s. 8d. Grants amounting to £150 had been made to Fellows from the Research Fund during the year.

Dr. GLADSTONE, F.R.S., proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Dr. STEVENSON, and carried.

The TREASURER, in responding, proposed a vote of thanks to the auditors.

Dr. ATKINSON seconded the motion, which was unanimously adopted, and acknowledged by Mr. R. J. FRISWELL.

Mr. D. HOWARD proposed a vote of thanks to the Officers and Council.

Mr. CASSAL seconded the motion, which was unanimously adopted.

Prof. THOMSON, F.R.S., responded on behalf of the Council.

Dr. B. DYER proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Mr. R. J. FRISWELL, and carried.

Mr. GROVES, F.R.S., responded.

The scrutators having presented their report to the President, he declared that the following had been duly elected:—

President—James Dewar, M.A., LL.D., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; Sir E. Frankland, K.C.B., D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, G.C.B., LL.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—F. R. Japp, M.A., LL.D., F.R.S.; G. D. Liveing, M.A., D.Sc., F.R.S.; William Ramsay, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, M.D., D.Sc., F.R.S.; John M. Thomson, F.R.S.; William A. Tilden, D.Sc., F.R.S.

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List of Fellows.

A new list of Officers and Fellows of the Chemical Society being in course of preparation, it is requested that Fellows will send any alteration of address, without delay, to the Assistant Secretary, Burlington House, London, W.

NOTICES OF BOOKS.

The Calorific Power of Fuels, founded on Scheurer-Kestner's "Pouvoir Calorifique des Combustibles." With the addition of a very full Collection of Tables of Heats of Combustion of Fuels, Solid, Liquid, and Gaseous. To which also is appended the Report of the Committee on Boiler-tests of the American Society of Mechanical Engineers (December, 1897); Tables of Constants used. By HERMAN POOLE, F.C.S., Member of [several Learned Societies], First Edition, First Thousand. New York: John Wiley and Sons. London: Chapmand and Hall, Ltd. 1898. Pp. xv.—255. 8vo. Illustrated.

THE author first planned a mere translation of Scheurer-Kestner's "Pouvoir Calorifique des Combustibles," but he found it necessary to make so many changes to adapt it to American methods and data that he retained only the skeleton of the French treatise, and filled this in from other sources. In the Introduction he adopts the usual classification and definition of fuels, and then explains the difference between calorific power and heat of combustion. He discusses the method of determining the heat of combustion, and then treats the subject of calorimetry quite exhaustively. The divers forms of calorimeters and the manner of using them occupy four chapters; following these are chapters on solid, liquid, and gaseous fuels. Chapter X. deals with the calorific power of coal burnt under a steam boiler; Chapter XI. treats of air supplied and gaseous products of combustion; and Chapter XII. explains the method of calculating the heat units.

In the Appendix is the Report named on the title-page and fifteen tables of constants. Following these are fuel tables, giving analyses of a large number of fuels of the three classes, together with their heat units and the authorities. The coals in these tables are from the chief beds in the United States, as well as in Nova Scotia, Ontario, Chili, France, Great Britain, Austria, Hungary, Germany, Spain, Russia, and New Zealand. Lignites and oils from America and abroad are treated in similar tables. An Index closes a well-printed volume, which is quite free from typographical errors, though "fuzed" (page 176) is an unusual way of spelling fused.

The work will undoubtedly prove of service to those engaged in the examination of fuels and the determination of their economic value.

Quantitative Chemical Analysis by Electrolysis. By ALEXANDER CLASSEN in co-operation with WALTER LÖB. Authorised Translation. Third English, from the Revised and greatly enlarged Fourth German Edition, by WILLIAM HALE HERRICK and BERTRAM B. BOLTWOOD. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1898. Pp. xii.—301. 8vo.

THIS standard treatise, by the Professor of Electro-Chemistry in the Royal School of Technology at Aachen, revised by the Lecturer on the same subject, differs from the earlier editions by the insertion of a Section devoted

to the ion theory. Faraday's law, Ohm's law, the significance of tension, of current strength and of resistance, as well as the theory of electrolytic precipitation, are all clearly explained. The various forms of voltameters, galvanometers, and the ampèremeter for measuring the current strength, and the voltmeter and electrometer for measuring tension, are well described and illustrated. Under the caption "sources of current" the authors describe the divers forms of cells, storage batteries, electro-magnetic machines, and thermo-electric piles.

A very practical chapter (not numbered) gives instructions for carrying on the process of analysis, with numerous woodcuts showing disposition of the apparatus: the translators have here inserted an account of von Malapert's apparatus.

A brief historical sketch of the development of electrolysis is rather singularly placed, being between chapters on the process of analysis and arrangements for analysis; credit is given to F. W. Clarke, Edgar F. Smith, and W. Gibbs, for their improvements and discoveries.

The former and the present equipment of the Electrochemical Institute of the Technical High School at Aachen are explained in detail, and illustrated with three full-page reproductions of excellent photographs. In Section II., also called "Special Part," the quantitative methods of determining metals and of their separation are described; at the beginning of each Section twelve to twenty references to literature are given—a valuable feature for those desirous of consulting original papers. In the Appendix are supplied examples for instruction. The book closes with two indexes.

The authors, translators, and publishers deserve credit for jointly producing so valuable and handsome a volume.

H. C. B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 3.

An Apparatus for Facilitating the Separation of the Natural Organic Principles.—C. Chabrié.—This paper cannot be understood without the accompanying diagram.

A Double Carbonate of Soda and Protoxide of Chromium.—G. Bauge.—If to a well-washed and still damp chromous acetate we add a solution of carbonate of soda in boiled water, we see that the acetate immediately goes into solution, and that almost immediately a reddish brown body is precipitated. This precipitation must be carried on in an atmosphere of carbonic acid perfectly free from oxygen. This sodic chromous carbonate forms two hydrates, one containing 10 molecules of water and the other 1 molecule. The former is a reddish brown powder, showing lozenge-shaped crystals under the microscope; it is an energetic reducing agent; it decomposes water below 100°, giving off hydrogen. In vacuo it loses water at the ordinary temperature; at 100° it forms the 1 molecule hydrate. Dilute sulphuric and hydrochloric acids dissolve it, giving blue solutions. The salt with 1 molecule of water is a yellow powder, with very similar properties to the other one; heated in vacuo or in a current of hydrogen it changes its colour to a dark brown, becoming yellow again on cooling. Cold boiled water gradually changes it into the salt with 10 molecules of water; when heated in a current of chlorine it gives chloride of chromyl. Analyses give these two compounds the following formulæ:—

$$CO_3CrCO_3Na_2 10H_2O.$$
$$CO_3CrCO_3Na_2H_2O.$$

Decomposition of Chloroform, Bromoform, and Chloral by an Aqueous Solution of Potash.—A. Desgrez.—Not suitable for abstraction.

Preparation of Carbide of Sodium and Monosodic Acetylene.—C. Matignon.—To prepare monosodic acetylene a current of dry acetylene is drawn through a flask containing sodium; from thence first into an empty flask and then into a large flask containing glycerin; the flask containing the sodium is placed on an oil-bath, and as soon as the sodium begins to melt the flask is shaken; the reaction then proceeds regularly, still shaking the flask and plunging it into the oil from time to time to keep up the temperature, which should be 180°. The sodium becomes gradually pulverised, and the reaction is at an end when it appears as a white homogeneous powder. To prepare carbide of sodium the same apparatus is used, but the operation is much quicker; the temperature is rapidly brought up to 220°, and kept at from 220—230°; the monosodic carbide which forms below 200° is then decomposed by the sodium not yet attacked—

$$C_2HNa + Na = C_2Na_2 + H.$$

Action of Sodium on Acetylene.—C. Matignon.—Between its melting-point and 190° sodium decomposes acetylene, $C_2H_2 + 2Na = C_2NaH + H$. Above 210° both the atoms of hydrogen are substituted and carbide of sodium is formed, $C_2H_2 + Na_2 = C_2Na_2 + H_2$. From 210—220° monosodic acetylene is decomposed—

$$2C_2HNa = C_2H_2 + C_2Na_2.$$

At the same temperature sodium transforms monosodic acetylene into disodic acetylene—

$$C_2HNa + Na = C_2Na_2 + H.$$

All these reactions take place quantitatively, producing pure, perfectly white bodies. At 300° acetylene no longer acts on a 2 per cent sodium amalgam.

Contribution to the Study of the Sulphonic Derivatives of Camphor.—A. Reychler.—In this paper the author describes at great length the only practical way of effecting the sulphonation of camphor. He has principally studied crystallised camphosulphonic acid and described some of its most important derivatives. By its oxime it would probably give rise to a sulphonic campholenic acid. Under the influence of reducing agents it should give interesting thio-derivatives.

MEETINGS FOR THE WEEK.

Monday, 18th.—Society of Arts, 8. (Cantor Lectures). "Sources of Commercial Indiarubber," by Dr. D. Morris, C.M.G.

Tuesday, 19th.—Royal Institution, 3. "Phases of Art—Past and Present," by T. C. Gotch.

Wednesday, 20th.—Society of Arts, 8. "Stage Mechanism," by Edwin O. Sachs.

—— Microscopical, 8. "On some Organic Substances of High Refractivity Available for Mounting Specimens for Examination under the Microscope," by H. G. Madan, M.A., F.C.S. "Instantaneous Photomicrography," by E. B. Stringer, B.A. At 7.30, an Exhibition of Diatoms, by H. J. Morland.

Thursday, 21st.—Chemical, 8. Ballot for the Election of Fellows. "The Carbohydrates of Barley Straw," by C. F. Cross, E.J. Bevan, and Claude Smith. "Isomeric Bornylamines," by M. O. Forster, Ph.D. "Some Derivatives of Benzophenone," by F. E. Matthews, Ph.D. "Researches on Camphoric Acid," by S. B. Schryver, Ph.D.

—— Royal Institution, 3. "Some Leaders in the Poetic Revival of 1760-1820—Cowper, Burns, and Scott," by The Rev. Canon Ainger, M.A., LL.D.

—— Society of Arts, 4.30. "Recent Railway Policy in India," By Horace Bell, M.Inst.C.E.

Friday, 22nd.—Royal Institution, 9. "The Recent Eclipse," by W. H. M. Christie, C.B., M.A., F.R.S., Astronomer Royal.

—— Physical, 5. "On a Method of Viewing Newton's Rings," by the Rev. T. C. Porter.

Saturday, 23rd.—Royal Institution, 3. "Programme Music" (with Musical Illustrations), by Sir Walter Parratt, Mus. Doc., Master of the Queen's Music.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2004.

SEPARATIONS FROM CHROMIC ACID.

III. The Separation of Aluminum.

By HARRY BREARLEY.

Reaction between K_2CrO_4 *and* Al_2Cl_6.

In a preceding paper (Chem. News, lxxvii., p. 49) it is stated, on the authority of Storer, that until five equivalents of potassium chromate have been added to a solution of ferric chloride, any precipitate formed locally is re-dissolved on shaking. This statement, using a solution of bar iron in aqua regia, I have not been able to verify. A precipitate forms much earlier than it should, and indeed can be made to form with variable amounts of chromate by suitably prolonging the addition of this reagent. The precipitates form much earlier in hot than in cold solutions.

These facts are in sharp contrast to the behaviour of aluminum (used as chloride). The reaction is formulated in a manner precisely analogous to that of iron—

$$Al_2Cl_6+5K_2CrO_4=6KCl+2K_2Cr_2O_7+Al_2O_3\cdot CrO_3,$$

and Storer and Eliot state similarly that no permanent precipitate is formed until five equivalents of the chromate have been added. This statement has been confirmed under just such conditions as with iron compounds would most emphatically refute it, viz., with a hot solution. In a cold solution the reaction proceeds very unsatisfactorily. Thus the precipitate formed almost from the first dissolves very tardily and never completely, except with very prolonged standing. If a slight opalescence be disregarded, and further addition of the chromate made, it can readily be seen that the precipitates are partly dissolved, but the turbidity which is apparently permanent continually increases, and is hardly effected by standing two or three hours, although only half the theoretical amount of chromate has been added.

Only so many of the properties of these basic chromates as are necessary to explain the respective separations need be noticed here; it has become evident that the strict analogy between them, insisted upon by Storer and Eliot, should be further examined.

Reaction between K_2CrO_4 *and* $Al_2(HO)_6$.

The aluminum hydrate (= ½ grm. Al) was prepared by adding an equivalent quantity of alkali to an acid solution of the chloride; in I. ammonium carbonate and in II. soda carbonate was used for this purpose, the chromate being added immediately after the alkali, and then the whole raised to boiling. There was recovered from the filtrates the amounts shown in—

Table VI.

K_2CrO_4 added.	Found in filtrate. I.	II.
10 c.c.	3·2	4·5
30 ,,	14·1	18·2
50 ,,	—	33·9

Relation of these Reactions to Analytical Methods.

Most of the methods previously noticed as being applied to the separation of iron are said to be also applicable to the separation of aluminum from chromic acid. A trial of several in turn was made; the results are collected into the following tables.

Separation with Ammonium Hydrate, Ammonium Carbonate, and Soda Carbonate.

In every case the alkali was two-normal strength; weight of Al, half a grm.; volume of K_2CrO_4 (1 c.c. = 0·05 Fe), 50 c.c. The arrangement of the results explain the details of the operations.

Table VII.

Excess of alkali.	Percentage separation. $(NH_4)HO$.	$(NH_4)_2CO_3$.	Na_2CO_3.
10 c.c.	89·0	81·3	94·0
20 ,,	90·5	93·6	95·3
30 ,,	93·1	94·4	99·0

The figures would seem to indicate the direction in which a perfect separation might be sought, but according to common knowledge the larger excesses of alkali would dissolve appreciable quantities of the precipitate $Al_2(HO)_6$. This defect is more marked with the soda than with the ammonia carbonate. One may therefore choose between leaving chromic acid in the precipitate or losing aluminum hydrate in the filtrate. Where the subsequent estimation of the elements is a gravimetric one the errors tend to balance each other, and for this reason may have seemed of less moment than they actually are.

Fresenius ("Quantitative Analysis," p. 294), after separating with ammonia or its carbonate, says, "If the washed alumina has a yellow colour, treat it on the filter with ammonia, and wash with boiling water; this will remove the last traces of chromic acid. A little alumina, however, dissolves in the ammonia, therefore heat the ammoniacal fluid in a dish until it has almost lost its alkaline reaction, and filter the separated flocks of alumina *to the principal precipitate*." It has been stated (Chem. News, vi., 182) that the basic chromates of alumina, when thoroughly washed, leave pure hydrate of alumina on the filter, but an acid chromate of alumina passes into the filtrate. If this is so, it is necessary *always* to examine the filtrate of an alkaline separation of aluminum and chromic acid. In any case the means proposed by Fresenius for recovering the dissolved alumina are open to the objection illustrated by Table VI., and the retention of this recovered alumina on the previously used filter tends to very considerably increase this error. On page 232 of the last edition of "Select Methods" one is instructed to separate alumina from chromic acid by adding ammonia, and boiling until the smell becomes very faint. The method is part of an electrolytic separation after Classen.

Separation with Soda Acetate.

Solutions of aluminum chloride, like solutions of ferric chloride, may be "neutralised,"—that is, they are able to re-dissolve their freshly precipitated hydrate. The extent to which this may take place has been carefully examined, and will be stated later; all we need remark now is, that under the most favourable conditions the—

$$xAl_2Cl_6.yAl_2(HO)_6$$

is more basic than the similar iron compound. From this it follows, if the solution be neutralised, that an acetate separation becomes subject to error, first, on account of the chromate's reaction with the chloride, and, second, on account of its reaction with the hydrate, which becomes precipitated as the chloride is decomposed.

Tests were made on solutions both with and without "neutralising." The filtrate from the samples not "neutralised" contained large quantities of alumina. This may be mostly due to the fact that the solutions were cooled before filtering (see Table I.), though partly it might be accounted for by the known solvent action of soda acetate, and the possible presence of acetic acid due to the decomposition of the precipitated aluminic acetate. The acetate contained 500 grms. of the crystallised salt per litre.

Table VIII.

Soda acetate.	Percentage separation. "Neutralised."	Not "neutralised."
20 c.c.	77·2	—
30 ,,	82·4	—
50 ,,	84·4	79·2
100 ,,	—	84·6
150 ,,	—	85·0

In each case the separation was of half a grm. of Al from 50 c.c. of the K_2CrO_4 solution in a bulk of half a litre.

Separation with Soda Phosphate.

This reagent was proposed by Carnot (Chem. News, xliv., 85). He operates on a solution slightly acidified with acetic acid. After adding an excess of phosphate the mixture is boiled and filtered. Those results in the table obtained on "unneutralised" solutions are precisely after Carnot's instructions. The solutions contained 1 per cent acetic acid (33 per cent).

Table IX.

Saturated solution soda phosphate.	Percentage separation. "Neutralised."	Not "neutralised."
20 c.c.	80·3	—
30 ,,	100·4	—
90 ,,	99·6	99·4
100 ,,	—	99·6
150 ,,	—	99·9

The 20 c.c. soda phosphate was unable to quite precipitate the half grm. of aluminum, although a clear solution was obtainable by repeated filtration.

These illustrations do not exhaust the number of methods which have been applied to the separation of the two bodies, but they sufficiently show that a compound so feeble as to be decomposed by merely washing may yet withstand the attack of strong precipitants.

In steel analysis only very small amounts of alumina and chromic acid come to be separated, and the defects are correspondingly insignificant. Even here, however, the use of ammonia and its carbonate in minimum quantities should be justified or abandoned: there is always a danger attending the general use of those methods whose range of accuracy is very small. Those methods, too, in which the aluminum salt is decomposed and precipitated by a neutral alkaline salt are open to suspicion. The method by Wöhler in which the mixed Al_2O_3 and Cr_2O_3 are dissolved in HCl, treated with excess of soda hydrate, oxidised with chlorine, and finally precipitating the still dissolved alumina with ammonium carbonate, belongs to the class already typified in Table VII. In face of the strong tendency to form a basic aluminium chromate, no process in which the aluminium is precipitated from neutral solution can be judged accurate until it has experimentally been proved to be so. Those processes in which the chromic acid is precipitated from the mixed solutions have not been studied.

The Separation of $Al_2O_3+Fe_2O_3$ *from* CrO_3.

It may be noticed that none of the methods observed both with iron and aluminum are equally satisfactory with either. The frequency with which these oxides are associated makes such a method desirable. Neither soda hydrate nor soda carbonate could be used except in conjunction with further means of separating the dissolved alumina. Soda phosphate, which serves so well for aluminum, does not give good results if the ferric solutions are "neutralised," and the presence of even considerable quantities of acetic acid is not a great improvement. An explanation of the different behaviour of neutralised solutions of iron and aluminum seems to lie in the fact that, while heating favours the formation of basic ferric chromates, it prevents the formation of the like aluminic compounds.

By ordering the solution so that only the free acid be neutralised and no dissolved ferric hydrate formed—this point is sufficiently indicated by the change of colour from yellow to reddish—the separations are accurate. This process tested with 0, 2, and 5 per cent of acetic acid acid present, and on the usual mixture of Fe_2Cl_6 and K_2CrO_4, gave recoveries of 99·8, 99·9, and 99·6 per cent respectively.

Totley, near Sheffield.

ON NASCENT HYDROGEN.

By D. TOMMASI.

Some years ago (*Comptes Rendus de l'Institut des Sciences de Milan*) I was occupied with the question as to whether the reducing properties peculiar to hydrogen, when set free from combination, are due to an allotropic state of the hydrogen, such as the nascent state, or to ordinary hydrogen under novel thermic conditions.

I studied the greater part of the reductions caused by hydrogen, which are generally but erroneously attributed to its nascent state, such as:—The reduction of the chloride, bromide, and iodide of silver; of chloric acid and the chlorates; of perchlorate of potassium; of the nitrates, &c.; and I here give in brief the results I obtained:—

1. Chloride of silver, in suspension in water acidulated with sulphuric acid, was treated with sodium amalgam. The experiment, which lasted forty minutes, was carried out in the dark. The chloride of silver remained perfectly white, and consequently had undergone no reduction; further, the liquid separated from the chloride of silver contained no trace of chloride of sodium. It is exactly the same with the bromide and the iodide of silver. On the other hand, a current of electricity will decompose the chloride of silver in suspension in acidulated water. In face of this, how can we explain why the chloride of silver, which resists the action of the nascent hydrogen produced by the decomposition of water by sodium amalgam, is reduced by the equally nascent hydrogen produced by the decomposition of the water by the electric current.

2. A saturated solution of chlorate of potassium was acidulated with sulphuric acid, then divided into two parts. One part was treated with zinc, the other with sodium amalgam; both reactions were stopped at the same time, while there was still some zinc and sodium amalgam left, and before the sulphuric acid was completely neutralised. The two solutions were filtered, and nitrate of silver was added. The solution which had been treated with the zinc gave a very abundant precipitate of chloride of silver, while the other solution, which had been treated with sodium amalgam, remained perfectly limpid. Chloric acid, and the chlorates of sodium, barium, copper, lead, and mercury undergo no reduction by sodium amalgam, whether we conduct the experiment in alkaline, neutral, or acid solution. Hydrogen formed by the electrolysis of water has no greater tendency to deoxidise chlorate of potassium.

3. A solution of perchlorate of potassium, chemically pure, was submitted to the action of various reducing agents, and the following results were obtained:—

(*a*). Perchlorate treated at the ordinary temperature, by zinc and dilute sulphuric acid, is not transformed into chloride, even when the solution is warmed.

(*b*). Magnesium and dilute sulphuric acid do not reduce the perchlorate, either hot or cold.

(*c*). A certain quantity of perchlorate was dissolved in a concentrated boiling solution of sulphate of copper; a piece of zinc was plunged into this,—immediately a violent reaction was produced, with a lively disengagement of hydrogen, but the perchlorate underwent no reduction. Neither is the perchlorate reduced when treated with

sodium amalgam, or with zinc and potash, warm, &c., or, in a word, by any of the principal reducing agents in ordinary use.

Now this perchlorate which has resisted all reduction, although in the presence of nascent hydrogen, is easily transformed into chloride by the action of a compound which does not give off hydrogen, viz., hydrosulphite of sodium. Although by the action of zinc on bisulphite of sodium (a reaction which gives birth to hydrosulphite of sodium) no hydrogen is given off; let us admit, for the sake of argument, that, on the contrary, there is. But then how could we explain that this same perchlorate, which experiences no reduction by nascent hydrogen in a large number of reactions, can be reduced by the hydrogen set free by the action of zinc on bisulphite of sodium? And why should nascent hydrogen, produced by the action of zinc on dilute sulphuric acid, reduce chlorate of potash and have no action on the perchlorate?

In these last two cases is it not always hydrogen in the nascent state which is given off? and the medium in which it is produced, is it not the same?

4. A solution of sulphate of nickel, even very dilute, to which potash and cyanide of potassium have been added, acquires a beautiful red tint by the action of zinc; at the same time hydrogen is given off. If in this experiment we replace the zinc by magnesium, or, better still, by the magnesium-platinum couple, we still notice the disengagement of hydrogen, but the red colouration is no longer produced. On the other hand, if the double cyanide of potassium and nickel is electrolysed, the red colour appears at the negative pole.

This must be due to one of two things:—either the red compound is produced by the metal or else by the nascent hydrogen.

In the former case the red tint should not be produced by the action of the hydrogen formed by the electrolysis of the water, and in the latter case it ought to be seen, since the hydrogen given off by the magnesium-platinum couple is just as *nascent* as that given off by the zinc or by the electric current.

5. S. Kern observed that, by causing magnesium to react on ferric chloride, ferric hydrate was produced. The note in which this observation was made was published by the *Bulletin de la Société Chimique de Paris* (vol. xxvi., p. 338), but the editor took care to add "but it does not appear probable that ferric hydrate should be produced, as there is a disengagement of hydrogen, or at least if there is no intervention of air."

I have repeated this experiment, taking care to keep all air away, and using only boiled water; but the results I obtained have always been identical with those of Kern. It is exactly the same if we substitute sodium amalgam for the magnesium.

6. According to the experiments of Stalschmidt, the nascent hydrogen produced by the decomposition of the water by powdered zinc transforms the nitrate of potassium into nitrite, the red cyanide into the yellow; it reduces the iodide and the iodates, but it does not reduce the chlorides.

7. De Wilde has stated that while sodium amalgam reduces bromate of potassium, it has no action on the chlorate.

In this latter case, as in the preceding one, is it not always nascent hydrogen which is given off?

If, then, the properties of nascent hydrogen were inherent to this allotropic state of the gas, we always ought to obtain the same reactions; but the experiments I have just quoted, and many others which I have passed over in silence, prove, on the contrary, that the reducing power of nascent hydrogen varies according to the chemical reaction which has produced it. And if this gas in the nascent state possesses a greater affinity than in the ordinary state, that is caused simply by the fact that the hydrogen, at the moment of being set free, is accompanied with all the heat which is produced while it is being set free.

Consequently, nascent hydrogen is synonymous with H + cal., and the differences that we observe between hydrogen produced by different chemical reactions have their reason in that these reactions do not all give off the same quantity of heat.

In fact, if we represent nascent hydrogen by H + a (a being the quantity of heat given off by the chemical reaction which produces the hydrogen), we shall get for a the following values:—

Chemical reaction.	Heat produced (a).
SO_4H_2 + Aq + Zn	38·0 cals.
SO_4H_2 + Aq + Cd	23·8 ,,
SO_4H_2 + Aq + Mg	112·0 ,,
2HCl + Aq + Zn	34·2 ,,
2HBr + Aq + Zn	34·2 ,,
Sodium amalgam + Aq	112·0 ,,

As can be seen, the value of a varies with each chemical reaction, and consequently the hydrogen should be the more active as the value of a increases, bearing in mind that *the reaction between the hydrogen and the substance to be reduced or to be hydrogenised may have commenced.* (In a future note I shall show that without this clause the principle of maximum work is quite wrong). There are, however, some cases when the reduction is not due to H + cal., but to the metal serving for the disengagement of hydrogen (M + cal.). Such is the case in the reduction of potassium chlorate by zinc and dilute sulphuric acid, or by the electrolysis of its solution using zinc as an anode.

In fact, when we electrolyse a solution of chlorate of potassium to which a few drops of sulphuric acid have been added, we obtain, according to the nature of the anode, an oxidation or a reduction of the salt.

Platinum Electrodes. — Perchloride is formed at the anode, without a trace of chloride at the cathode.

Platinum Cathode and Zinc Anode.—Chloride of potassium is formed *only at the anode*, with not a trace at the cathode.

The reduction of the chlorate in this case cannot be attributed to hydrogen, but to the zinc, which unites with the oxygen of the chlorate, forming oxide of zinc according to the equation $KClO_3 + 3Zn = KCl + 3ZnO$.—*Moniteur Scientifique*, Series 4, vol. xii., March, 1898.

ON A SIMPLE METHOD OF PREPARING HYDRONITRIC ACID.

By M. DENNSTEDT and W. GÖHLICH.

Some time ago one of us put forward the opinion that the properties of argon, if we considered this gas as triatomic nitrogen, could be explained up to a certain point by admitting a central bond between the atoms of nitrogen. Although subsequent researches have left no doubt as to the elementary nature of argon, we nevertheless thought it interesting to submit our supposition, as far as could be done, to experimental verification. In hydronitric acid we have already a cyclic liaison of the atoms of nitrogen, and it seemed possible by carefully arranged oxidation to eliminate the atom of hydrogen, leaving intact the nucleus of three atoms of nitrogen.

Experiment has shown that the gas obtained by oxidising hydronitric acid by permanganate of potash in the presence of sulphuric acid in an atmosphere of carbonic anhydride is nitrogen, and not argon. The hydronitric acid necessary for this experiment was prepared by a very simple process, which enables one to obtain a dilute solution of the acid in any desired quantity in a few minutes. Admitting that the dilute acid can be easily concentrated by distillation, our process applies equally to the preparation of the concentrated acid. This process is very convenient as a lecture or class experi-

ment, as by its use we can prepare hydronitric acid from inorganic substances; it being a serious inconvenience to have to use, in the early lessons on inorganic chemistry, complex organic substances in order to prepare such a simple inorganic compound as hydronitric acid.

Curtius (*Berichte*, 1893, p. 1263; *Ibid.*, 1890, p. 3023) has already pointed out the possibility of obtaining nitramide by the action of nitric acid on hydrate of hydrazin, but this method has always given us very poor returns, so that we do not consider it advisable even for the preparation of small quantities of hydronitric acid.

At the commencement of his first memoir, Curtius says:—"In the same manner that the action of nitrous acid on ammonia gives rise to the formation of nitrogen and water, so should the action of the nitrites on monochlorhydrate of hydrazin gives rise to the formation of hydronitric acid,—

$$NH_4Cl + NO_2Na = N_2 + 2H_2O + NaCl$$

$$\begin{matrix} NH_2HCl \\ | \\ NH_2 \end{matrix} + NO_2Na = \begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!NH + 2H_2O + NaCl."$$

However, it appeared to be difficult to prepare hydronitric acid, starting directly from hydrazin and nitrous acid; in fact, under these conditions we were unable to obtain it.

The formula of the monosulphate of hydrazin is $(NH_2,NH_2)_2,H_2SO_4$. If we distil a mixture of monosulphate of hydrazin and nitrite of potash in aqueous solution, there passes—without any preliminary disengagement of gas—first a trace of hydrazin and no ammonia, after which the quantity of hydrazin increases, and at the same time a little ammonia comes over, and finally the hydrazin disappears entirely, to give place to the ammonia.

The monosulphate of hydrazin is thus decomposed under these conditions into hydrazin and ammonia without the formation of any hydronitric acid.

The bisulphate, however, behaves quite differently. Commercial sulphate of hydrazin is the secondary salt $(NH_2,NH_2)H_2SO_4$. This salt should react with nitrite of potash according to the following equation:—

$$N_2H_4,H_2SO_4 + KNO_2 = NH_3 + KHSO_4 + 2H_2O.$$

If to a solution of sulphate of hydrazin (5 grms.) we add a solution of nitrite of potassium (3·3 grms.) in about 200 c.c. of water, a lively disengagement of gas takes place, which only diminishes very slightly even when the solution is reduced to a very low temperature. We at first thought that this gas was nitrogen, resulting from the decomposition of the hydronitric acid formed; but later we satisfied ourselves that the reaction was effected in quite a different manner. If the liquid is distilled after the gas has ceased to come off a considerable quantity of hydronitric acid passes over. It is easy to concentrate the dilute acid by repeated distillations. The return is more satisfactory when the two solutions have been thoroughly cooled before mixing. Commercial nitrite of potassium contains a considerable quantity of free alkali, and it is of importance to exactly neutralise the alkalinity, or better still to add at once the quantity of sulphuric acid necessary to combine with the free alkali and set free the nitrous acid. The return obtained from 5 grms. of sulphate of hydrazin rises then to 0·2 grm. of N_3H, while the disengagement of gas does not diminish to any appreciable extent. It results from this fact, that the disengagement of gas is not a secondary phenomenon, but constitutes an essential factor of the reaction. The analysis of the gas given off shows that it consists of nitrogen, oxygen, and protoxide of nitrogen. Although the quantitative analysis of a mixture having such a composition offers certain difficulties, we have succeeded in estimating the oxygen approximately, by absorbing it by pyrogallate of potash, the protoxide of nitrogen by repeated absorptions by water, and the nitrogen by difference.

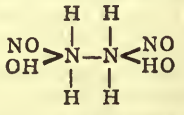
The nitrogen, we might mention, did not contain any argon. The results of our analyses have led us to believe that the formation of hydronitric acid takes place according to the following equation:—

$$3N_2H_4H_2SO_4 + 6KNO_2 + 3H_2SO_4 = 2N_3H + 8H_2O + 6KHSO_4 + 2O + 2N + 2N_2O.$$

According to this equation, 3 grms. of sulphate of hydrazin should furnish 1·1 grm. of hydronitric acid; but we were only able to obtain 0·2 grm., or 20 per cent of the theoretical quantity. Further, the volumes of the oxygen, the nitrogen, and the protoxide of nitrogen ought to be in the ratio 1 : 1 : 2. Now, we have always found twice the calculated volume of nitrogen, and a little less oxygen than there should be. This can only be accounted for on the supposition that a part of the oxygen set at liberty oxidises a part of the hydronitric acid formed into water and nitrogen. As for each volume of oxygen which takes part in the reaction, six volumes of nitrogen are formed, the result we have obtained is explained in a very simple manner. It is evident that the formation of hydronitric acid, starting from secondary sulphate of hydrazin, should follow quite a different path than that indicated by Curtius in his experiment with monochloride of hydrazin and nitrite of soda. In this reaction with three soda atoms, the hydronitric acid ought to be formed from the nitrogen of the hydrazin and that of the nitrous acid, while in our reaction the whole of the nitrogen of the nitrous acid is eliminated in the state of free nitrogen and protoxide of nitrogen; the nitrogen in the hydronitric acid formed being furnished exclusively by the hydrazin. We can illustrate this method of the formation of hydronitric acid in the following manner:—Sulphate of hydrazin and nitrous acid first gave rise to the formation of nitrite of hydrazin:—

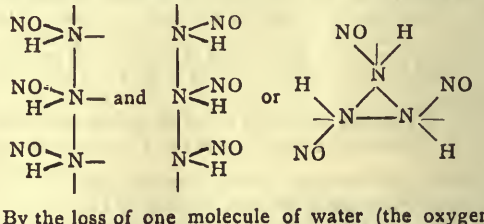
$$HNO_2,NH_2—NH_2,HNO_2$$

or—

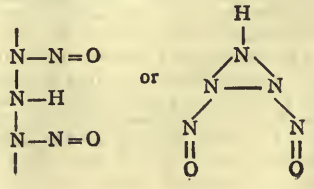


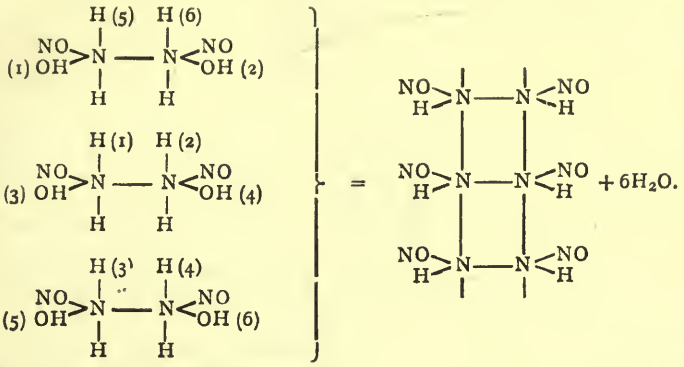
As with all the ammonium salts, the nitrogen is pentavalent in this compound. In the next phase, three molecules of the slightly stable nitrite of hydrazin form a cyclic compound by eliminating six molecules of water. The hydroxyl groups and the atoms of hydrogen which unite to form water are indicated in the formula by the same figures. (See formula, next page).

By breaking the bonds between the atoms of the hydrazinic nitrogen, two new molecules are formed—unsaturated, and therefore unstable—which already enclose three atoms of nitrogen re-united in a cyclic nucleus.

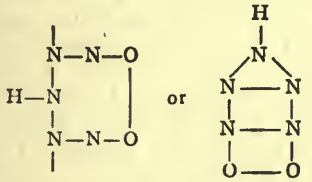


By the loss of one molecule of water (the oxygen is supplied by the group NO, nitrogen being given off at the same moment) there is formed—





This intermediate compound can also be expressed by the formula—



which takes account of the subsequent elimination of the protoxide of nitrogen and the oxygen. This elimination leads to the formation of hydronitric acid. It is well understood that the above phases may take place simultaneously.—*Chemiker Zeitung*, p. 876, 1897).

ON THE AMMONIA TEST OF COCAINUM HYDROCHLORICUM ACCORDING TO MACLAGAN.

By Messrs. C. F. BOEHRINGER and SOEHNE, Waldhof, near Mannheim.

In No. 1 of the *Pharmaceutische Centralhalle*, January 6, 1898, Dr. Fritz Günther inquired into Maclagan's ammonia test, the result of his investigation being:—

1. The occurrence of Maclagan's reaction depends on chance, and the test, therefore, is unreliable.
2. It is not known what impurities are to be demonstrated by this reaction.
3. It is established that there is no difference in physiological action between a cocaine fulfilling the requirements of the German Pharmacopœia III., which shows the reaction, and a cocaine which does not show it.

We consider it our duty to reply to this condemnation of Maclagan's test, the great value of which in testing commercial cocaine we have recognised for many years past, owing to the fact that a preparation not standing this test contains a larger amount of the admittedly toxic isatropylcocaine than should be permissible nowadays for medical use.

This circumstance, having long since come to the knowledge of the parties interested, it is all the more surprising to us how a cocainum hydrochloricum, containing a considerable percentage of isatropylcocaine, placed on the market by an otherwise renowned firm, could find a sale. We can explain this only by assuming that buyers relied on the manufacturer's good reputation, and that they were content with the fact of the preparation complying with the requirements of the Pharmacopœia. Thus the efforts of manufacturers to put within reach of medical men the purest possible preparations are practically useless, until the Pharmacopœia Committee recognises that something better than hitherto admissible is within reach, and issue stricter regulations for testing the remedy concerned.

We will now try to prove the strength of the reasons in favour of Maclagan's test, and the weakness of the arguments adduced against this otherwise generally recognised test by Dr. Günther in favour of the inferior preparation.

Whereas Maclagan states that an amount of 4 per cent of by-alkaloid (when publishing his test in 1887 Maclagan did not know of the existence of isatropylcocaine) causes a milky turbidness of the liquid, manufacturers of cocaine are well aware of the fact that it is isatropylcocaine which in the ammonia test prevents a crystalline precipitate of the cocaine.

In order to demonstrate that this impurity exists in the above-mentioned commercial preparation, we indirectly bought ½ kilogrm. thereof and tested it.

One hundred grms. of this cocainum hydrochloricum were dissolved in water, precipitated by a solution of soda, and dried. The alkaloid was dissolved in absolute alcohol, the alcoholic lye, after cooling, was drawn off from the precipitated cocainum purum, and evaporated to dryness at a moderate heat.

By repeatedly treating it with petroleum ether (see Liebermann, "Report of the Deutsche Chem. Gesellschaft," 1888, p. 2343) we succeeded in isolating from the residue 3·6 grms. of an alkaloid very difficult of solution in petroleum ether. To demonstrate its really being isatropylcocaine, it was split up according to Liebermann's method, by concentrated hydrochloric acid ("Report of the Deutsche Chem. Gesellschaft," 1888, p. 2346), whereby we obtained 1·1 grm. of crude isatropa-acid, which, by treatment with a solution of barytes on the one hand, was converted into the readily soluble barytes salt of the γ-isatropa-acid; on the other hand, into the δ-isatropa acid (the latter soluble with difficulty). After being but once re-crystallised from alcohol, the isolated acids from both salts showed the melting-points given by Liebermann, viz., 274° C. for the γ-acid and 206° C. for the δ-acid.

Thus it is proved that the cocaine in question contains at least 3·6 per cent of isatropylcocaine, probably more.

This cocaine does not stand Maclagan's test, and shows at once, on addition of the ammonia, a milky opalescent turbidness, indicating, according to Maclagan, a minimum amount of 4 per cent of by-alkaloid.

In order to ascertain more accurately the influence of the isatropylcocaine on Maclagan's test, we made up the following mixtures of pure hydrochlorate of cocaine* with hydrochlorate of isatropylcocaine,† 0·1 grm. to 87 c.c. of water, as we were accustomed to do, and tested each one after the addition of four drops of ammonia (sp.

* This cocaine stands Maclagan's test. After the addition of four drops (=0·2 c.c.) of ammonia (sp. gr. 0·95), followed by stirring for one and a half minutes, an intense crystalline precipitate took place, which pervaded the whole liquid.

† Obtained from the crude alkaloid by frequently boiling it with petrol ether.

gr. 0·96) as to its behaviour, vigorously stirring the liquid with a glass rod in a stout glass vessel, and pressing it from time to time against the walls of the vessel.

The following reactions ensued :—

	Per cent isatropylcocaine.		Minutes.	
1.	0·0	Crystalline precipitate after	1½	Liquid clear at first.
2.	0·1	,, ,, ,,	2½	
3.	0·2	,, ,, ,,	5	
4.	0·4	Amorphous ,, ,,	6	
5.	0·6	,, ,, ,,	5	
6.	0·8	,, ,, ,,	8	
7.	1·0	Hardly visible ,, ,,	10	
8.	2·5	None.		
9.	3·5	,,		
10.	4·0	Liquid slightly opalescent.		
11.	5·0	,, milky turbid.		
12.	10·0	, very ,,		

Accordingly, by means of Maclagan's test, a cocaine containing no isatropylcocaine or less than 0·2 per cent thereof, can be clearly distinguished from a more impure cocaine.

It is true that a cocaine containing 0·2 per cent of isatropylcocaine can hardly be distinguished from cocaine containing 1 per cent; hence the so-called irregularities exhibited in this test, for the very reason of its requiring a very pure cocaine. At all events, in this test a pure preparation must fulfil the requirements of showing in any case a considerable precipitate within from one to three minutes, perhaps after five minutes—dependent on the vigour in stirring.

If containing more than 1 per cent of isatropylcocaine —up to 4 per cent—the liquid remains clear on the addition of ammonia, but even after a quarter of an hour's vigorous stirring and pressing it does not show a crystalline precipitate worth mentioning. Not until the amount is 4 per cent does a slight opalescence appear after the addition of ammonia. With an amount of 5 per cent and more of isatropylcocaine the liquid becomes distinctly milky.

Regarding the size of the drops of ammonia, said by Dr. Günther to greatly influence the test, we beg to say:—For 0·1 grm. cocainum hydrochloricum there is theoretically necessary 0·05 grm. of an ammonia solution of 0·96 sp. gr. (containing 10 per cent of ammonia); 3 drops usually correspond to three times this quantity = 0·15 c.c. (20 drops = 1 c.c).

This quantity, therefore, is sufficient, and the drops must be proportionately large.

According to the experiences we daily acquire regarding our own product, cocainum hydrochloricum, if containing less than 0·2 per cent of isatropylcocaine, stands Maclagan's test upon the addition of from 3 to 4 drops of ammonia. A considerable crystalline precipitate is deposited, which at the moment of forming pervades the whole liquid. (In the ammonia glass vessel generally used by us we found 4 drops to be equal to 0·2 c.c.).

According to "Commercial Organic Analysis" (Allen, vol. iii., Part 2, p. 280), Maclagan, moreover, suggests to take for 1 grain (=0·0648 grm.) 2 drops of strong ammonia. By this none other can be meant than ammonia of a sp. gr. of 0·901 = 28 per cent, mentioned in the United States' Pharmacopœia under the heading of "Stronger Ammonia Water." Hence follows that for 0·1 grm. 3 drops of a 28 per cent ammonia solution should be taken,—therefore about 8 to 9 drops of a 10 per cent ammonia solution of a sp. gr. of 0·96, according to the German Pharmacopœia; whereas in our experience 0·2 c.c. of the 10 per cent ammonia solution is sufficient, that is, much less than mentioned by Maclagan. Sufficient ammonia, of course, to liberate the base must be present.

Summing up our opinion on Maclagan's test, we find that it very well admits of an accurate examination of cocainum hydrochloricum in reference to the amount of isatropylcocaine, if the following points are strictly observed :—

1. For 0·1 grm. of cocainum hydrochloricum at least 0·15 to 0·2 c.c. of ammonia of a sp. gr. of 0·96 must be used.
2. Very vigorous stirring in a stout glass vessel is necessary, as, according to our observation, even in perfectly pure cocaine, artificially prepared from ecnogin, a precipitate is but rarely obtained without stirring. The walls of the glass vessel should be pressed with the glass rod immediately after the addition of ammonia, say ten times to and fro, to be followed by vigorous whipping with the glass rod.

If thus treated the precipitate is sure to take place in cocaine containing less than 0·2 per cent of isatropylcocaine.

We would still mention that the proportion of 0·1 grm. of cocainum hydrochloricum to 100 grms. of water, as stated by Dr. Günther, does not agree with the proportion mentioned by Maclagan. It is true that, owing to the confusing significations of English and American ounces, fluid ounces, avoirdupois and medicinal weight, it is not easy to get at the respective equivalents in metrical weight. A grain is always = 0·0648 grm.; 2 ounces of water calculated as ounces weight may be = 2 × 31·104 grms., in which case the proportion would be 0·0648 : 62·208 = 0·1 : 96·0; but if calculated on the basis of the commercial weight (1 ounce = 28·35 grms.), the proportion is 0·1 : 87·3.

Taking the weight of an American fluid ounce = 29·570 c.c. (of water therefore = 29·570 grms.) the proportion is 0·1 : 91·3. Anyhow, Maclagan's intention cannot have exceeded the proportion of 0·1 : 96.

We have found, on the one hand, that even in pure cocaine the precipitate occurs with greater difficulty if the quantity of water is increased, and, on the other hand, that by less stirring of the liquid with the glass rod it takes more than five minutes for the precipitate to occur, even with pure cocaine in a solution of 0·1 : 100.

Now, in order to bring about a practical and clear definition of Maclagan's test, we propose to dissolve 0·1 grm. of cocainum hydrochloricum in 85 c.c. of water, and to add as many drops of ammonia (sp. gr. 0·96) as correspond to 0·2 c.c.

As to the third point of Dr. Günther's condemnation of Maclagan's test, viz., the physiological effect of cocaine rendered impure by isatropylcocaine, we beg to say :—

There is no foundation for Dr. Günther's assertion that in respect of physiological action there is no difference between a cocaine standing Maclagan's test and a cocaine which does not stand it; in his publication even opinions of medical authorities are not quoted in demonstration thereof. No doubt, however, can exist as to the toxic effect of isatropylcocaine, for after its discovery Prof. O. Liebreich examined the alkaloid, and Prof. Liebermann ("Report of the Deutsche Chem. Gesellschaft," 1888, p. 2344), in his paper thereon, says :—

"Professor O. Liebreich was good enough to examine the alkaloid in reference to its physiological effect. According to his communication the alkaloid in question is of interest also, owing to its great toxic effect, and owing to its probably being the cause of the toxic secondary phenomena repeatedly observed after the administration of cocaine not quite pure. Its effect resembles neither that of cocaine nor of atropine; it is rather a *strong heart-poison*. A decrease in sensibility was neither observable when applied locally nor generally."

In spite of the toxic effect of this by-alkaloid being known, a preparation containing 3 to 4 per cent thereof is put on the market, bought unhesitatingly, and supplied to medical men! And withal a pure preparation, and the means of testing it are available.

A conscientious manufacturer of cocaine, therefore, should endeavour to supply a pure product. This is not requiring too much seeing that the best brands of this article are so supplied.

As shown by us, the test necessary for ascertaining the absence of this dangerous impurity has been furnished by Maclagan, and, indeed, in a thoroughly satisfactory form, so that everybody desirous of placing on the market medicaments of the greatest possible purity, is enabled to do so as regards cocaine.

By the foregoing we think we have demonstrated the necessity of submitting commercial cocaine to Maclagan's test.—*Pharmaceutische Centralhalle*, 1898, No. 9.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 9th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined by us, all were found to be clear, bright, and well filtered.

There has been a still further serious deficiency in the rainfall in the Thames valley during the past month. The actual amount which fell at Oxford was only 0·66 inch; the average for 30 years is 1·50 inches, leaving a deficiency of 0·84 inch, and bringing the present deficiency for the year up to 2·75 inches. The total rainfall for the first quarter of this year is only 2·67 inches, or less than half the thirty years' average.

Our bacteriological examinations of 268 samples have given the results recorded in the following table; we have also examined 37 other samples, from special wells, standpipes, &c., making a total of 305 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	814
New River, filtered (mean of 27 samples) ..	28
Thames, unfiltered (mean of 27 samples) ..	3917
Thames water, from the clear water wells of five Thames-derived supplies (mean of 133 samples)	25
Ditto ditto .. .. highest	296
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	1193
River Lea, from the East London Company's clear water well (mean of 27 samples) . ..	24

The exceptionally dry weather is having the usual effect of keeping the river in good condition; this, in conjunction with the high efficiency of the filtering arrangements of the various companies, accounts for the purity of the water at present supplied to London.

The following comparison illustrates the improvement in chemical composition consequent on an abnormally low rainfall. The rainfall in March, 1897, was above the average:—

Comparison of the Averages of the Five Thames-derived Supplies for the Months of March, 1897 and 1898.

	Common Salt. Per gall.	Nitric Acid. Per gall.	Hardness.	Oxygen. reqd. Per gall.	Organic Carbon. Per gall.	Organic Carbon. Per gall.	Colour.
	Means.	Means.	Degrees. Means.	Means.	Means.	Max.	Means. Br'n: Blue.
March,							
1897.	2·018	1·035	17·12	0·064	0·152	0·196	17·2 : 20
1898.	2·167	0·877	16·06	0·033	0·076	0·109	10·9 : 20

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE DIGNITY OF ANALYTICAL WORK.*

By C. B. DUDLEY.

(Continued from p. 174).

ANOTHER illustration from a different field will emphasise the power of an analysis to explain difficulties. A lot of boiler plate was at one time received at Altoona shops, from one of the best makers. In this lot of forty or fifty sheets, two were found which gave difficulty in flanging, this operation consisting, as is well known, in bending over the edges of the sheets while hot, nearly at right angles to the balance of the sheet, in order to enable it to be joined to other sheets in the boiler. The two sheets referred to cracked in the bend, although the remainder of the lot gave no difficulty from this cause. The workmen being thoroughly experienced, and the practices of the shop being excellent, the cause of the failure in the case of these two sheets was not apparent. An analysis of samples from each of these sheets, however, showed 0·35 per cent and 0·36 per cent of carbon respectively, while analyses of samples from other sheets in the same lot showed in no case above 0·12 to 0·15 per cent of carbon. The explanation of the difficulty seemed now quite clear. The shops had been supplied for a long time with the softer grade of steel, and the methods and practices in use were those applicable to that kind of steel. No wonder, then, that with the harder grade difficulty should arise, as actually happened, and but for the analysis this might have passed into shop traditions as one of those unexplained and unexplainable crochets of steel which both the makers and practical users of this metal delight in constantly bringing forward.

A single illustration further will, perhaps, suffice on this head. A few years ago a shipment of some three hundred freight axles was received at two different shops on the Pennsylvania Railroad, from an entirely reputable maker. Some of these axles were used for repairs, and some went under new cars. Scarcely had they gotten into service, however, before difficulty began to arise. The axles began to break; indeed one of them broke before the car had been turned out of the shop yard, one broke into three pieces before the car had made 150 miles, and in less than three months eight had broken. Each of the broken axles was sent to the laboratory, and a careful study of the case made, with the hope of discovering the cause of the failure. An examination of the freshly fractured ends of several of the broken axles showed that for a little distance in from the circumference the fractured steel presented an appearance quite different from that given by the remainder of the fracture. Moreover, a line of demarcation between these two apparently different kinds

* Presidential Address delivered at the Washington Meeting of the American Chemical Society, December 29, 1897. From the *Journal of the American Chemical Society*, vol. xx., No. 2.

of steel in the same axle could be clearly traced. Accordingly it was decided to make analyses of borings from near the circumference and near the centre, and see whether this would reveal anything. It may be stated that the axles were known to have been made from Bessemer steel, and should normally have contained not more more than 0·10 per cent of phosphorus. The analysis of the borings from near the circumference of the axles in no case gave figures up to this limit, while the borings from the centre of the axles in no case showed less than 0·16 per cent phosphorus, and in some cases the amount was as high as 0·24 per cent. Those who are familiar with the methods in daily use in modern steel works will from these figures at once understand the cause of breakage of these axles. For the benefit of those who are not, it may be well to explain that in most modern steel works large ingots are now the rule, and that in large ingots which take considerable time to solidify from the molten condition analyses show that some of the constituents of the steel are not uniformly disseminated throughout the mass. This separation of the constituents during cooling, technically known as "segregation," is characteristic of the carbon, the phosphorus, and the sulphur. Furthermore, the segregation appears to be worst in the upper third of the ingot, so much so that many specifications now require the upper third of the ingot to be removed, and not used at all in making the articles the specifications call for. This much being stated, it is clear why our axles broke. They were made from badly segregated steel, perhaps from the rejected upper thirds of a lot of ingots the balance of which were used for other purposes. Subsequent correspondence with the parties furnishing the axles gave good grounds for belief that such was the case. For the comfort of those who ride on railroads it may be added that the three hundred axles were at once withdrawn from service, and that since that time a chemical and physical specification for both passenger and freight axles has been prepared, which is believed to preclude the possibility of such axles as are described above being received by the Pennsylvanian Railroad.

These illustrations of the power of an analysis to explain difficulties could be prolonged to almost any extent, but I spare you. Furthermore, I should not like to be understood as claiming that every puzzle, every difficulty, or every state of affairs in Nature, where the reasons for the phenomena which we find are not apparent at sight. can be explained by a chemical analysis. Our knowledge is far too limited for this. Moreover, many cases could be cited in which an analysis throws no light whatever on the situation; but notwithstanding this, an experience of some twenty years in seeking out the causes of things, as a necessary preliminary to the intelligent modification of practices and methods, in connection with a great corporation, has continually impressed me more and more with the very great help which a properly conceived and executed analysis can give in cases of difficulty.

But again I take pride in the field of analytical work, because of the opportunity which thoughtful analytical work affords for finding new things. The careful, thoughtful, observant analyst is constantly on the verge of either being able to add to his own knowledge, or of being able to contribute something to the general progress of our science. And here again I must be pardoned for using, as illustrations, cases which have arisen in the laboratory of the Pennsylvania Railroad Company.

A few years ago, in our laboratory, we began to get ready to make our analyses of the samples of steel which were designed ultimately to be the international standards for the analysis of iron and steel. Before starting in on these samples, however, it was deemed prudent to do a little preliminary work on some other samples, with the idea in mind of seeing whether apparatus and method were satisfactory. Accordingly four separate and distinct determinations on the same sample were made for carbon, using the double chloride of copper and ammonium to release the carbon, and burning in oxygen gas. The four determinations agreed with each other within 0·01 or 0·02 of a per cent, and were regarded as fairly satisfactory. But as the work was important, and as some parts of the apparatus had not worked quite satisfactorily, it was decided to repeat the four determinations. Meanwhile a new stock bottle of solution of the double chloride had been made exactly in the manner that had been our custom for some time previous. When the second four determinations were obtained, they differed from the first by more than a tenth of a per cent. I need not weary you with the details of our hunt for the cause of this discrepancy,— how every point in the apparatus was tested up one after another, how various modifications were tried, how combustions were made on crystallised sugar to check ourselves, and how finally we located the difficulty in the double chloride of copper and ammonium solution. These details have all been published (*Trans. Amer. Inst. of Mining Engineers*, xix., 614). Suffice it to say that as the result of this work, together with subsequent work by other chemists, it is, we believe, now generally accepted that the commercial ammonium double salt contains carbon in some form, probably pyridine, that its use as a solvent to release the carbon from iron and steel is unreliable, and that the substitution of the potassium for the ammonium double salt overcomes these difficulties. The point which I especially want to emphasise is, that in trying to do a little careful analytical work we struck a new and apparently hitherto unsuspected source of error in one of the oldest and best established methods of iron and steel analysis.

Another illustration will perhaps make this point still more clear. In the regular course of work at one time a silicon determination was made in a piece of tire steel, which had been sent by an officer of another railroad, for information. The figures found by our analysis were 0·14 per cent, these figures being sent to the officer above referred to. A little later, word was received that an analysis of a sample from the same tire, made by another chemist, gave 0·28 per cent as the content of silicon. This, of course, led us to look over our work, with the idea of finding where the cause of the discrepancy lay. A careful examination of our weights and figures showed that it was not an error of calculation. Accordingly we decided to duplicate our work, need I say with the expectation of finding that the other chemist had made a mistake? Judge of our surprise when we found that our second analysis confirmed his figures exactly. Our first and second analyses had been made by the same method, and by the same operator, working on borings from the same bottle, and the cause of the discrepancy between the two was not, therefore, at first sight apparent. On carefully questioning the operator, however, as to exactly what he did at each step of the method, a clue was obtained, which, when followed out, cleared up the whole difficulty, and ultimately led to a modification of the method. The silicon in these samples was determined by what is known as Drown's method, consisting in dissolving the steel in nitric acid, adding sulphuric, heating until white fumes of the latter acid appear, to render the silica insoluble, dilution with water, filtration, washing, and weighing. The difference between our two analyses consisted simply in this—that in the first case, after the dilution with water, there being considerable work in hand, the vessel was allowed to stand over night before filtration, while in the second case filtration immediately followed dilution. Subsequent work on this point showed that in this method silica is not completely dehydrated by heating in concentrated sulphuric acid, in presence of iron salts, but is apparently rendered colloidal and sufficiently dehydrated, so that, if filtration follows soon after dilution, fairly accurate results will be obtained. On standing after dilution, however, this colloidal, undehydrated silica apparently goes into solution again. Indeed we were able to get on this same sample,

anywhere from one-eighth up to the full amount of silicon present, by varying the time of standing after dilution, the longest time covered by our experiments being about four days.

(To be continued).

CORRESPONDENCE.

VOLUMETRIC DETERMINATION OF CHROMIUM IN IRON AND STEEL.

To the Editor of the Chemical News.

SIR,—In Mr. H. Brearley's article on "Separations from Chromic Acid" in your issue of March 25th (CHEM. NEWS, vol. lxxvii., p. 131), he draws attention to some possible errors in the volumetric determination of chromium in iron and steel as described by me in 1877 in the CHEMICAL NEWS (vol. xxv., p. 151), and in 1893 before the Iron and Steel Institution, for the consideration of which I would crave a little space.

The criticism is somewhat curious, and is, I think, due to a good deal of misapprehension. I do not know what objection Mr. Brearley refers to when he says "Galbraith deals with some objections which had been repeatedly urged against his method."

Referring to my paper of 1893, Mr. Brearley says:—"He might have reduced the needlessly large bulk of oxides by adding less permanganate, a procedure we had long before found to minimise the error." If he (who does Mr. Brearley mean by "we"?) found this out he has carefully kept it to himself (I knew it in 1878), but I am not aware of any explanation of it being given before that given by Mr. Stead and myself in 1893.

Again, he says—"but nowhere does he adopt the more satisfactory course of dissolving a pure carbon steel along with a known quantity of a chromium salt." I say in the paper—"I now tried the effect of the presence of iron," but this is without the use of soda. The experiments, as recorded below, fulfil those conditions, but there is no reason to suppose, unless Mr. Brearley's objection is correct, that the testing of it with a solution of chromic acid or bichromate solution was not a fair method of testing it, supplementing these with examples on actual chromium irons.

Let me remind Mr. Brearley, however, that the title of my paper in 1893 was "The Determination of Chromium in *Ferro-chromium*." I nowhere recommend the use of soda for chromium steel; it is not necessary, and quite accurate results can be got without it.

I regret that Mr. Brearley's paper is full of criticisms of the above character, because it is apt to disguise the fact that he has hit upon quite a likely source of error, and his paper otherwise is valuable.

His objection is that when soda is added to the sulphuric acid solution of chromic oxide in presence of the manganese salt got from the reduction of the added permanganate, the precipitated oxide of manganese reduces the chromic oxide.

I think he gives away most of his case, however, when he says that "when he reduces a standard solution of bichromate and treats it with potassium permanganate and soda, he gets fair results." And, moreover, when he adds that he has "made trials on artificial and actual examples of chrome steel, and have obtained results in keeping with above explanation," I might reply that he ought to have given the figures, and further, that the modification, as I have already explained, was not meant for chromium steel.

I have carried out the following experiments to ascertain if there is any reducing action such as he describes.

Fifty c.c. standard bichromate solution was made up to 100 c.c., and reduced with SO_2. Ten c.c. H_2SO_4 and 1 grm. $K_2Mn_2O_8$ was then added, and the solution boiled till the $K_2Mn_2O_8$ was entirely reduced. The solution was then diluted to about 250 c.c. and made alkaline with NaHO. It was then filtered and the insoluble matter washed, the filtrate made acid with HCl, 4 grms. $(NH_4)_2SO_4FeSO_46H_2O$ added, and the excess of Fe as FeO determined with bichromate.

As 1 grm. of the iron salt took ..	14·3 c.c.	$K_2Cr_2O_7$
4 grms. are equal to	57·2 ,,	,,
Less 50 c.c. used	50·0 ,,	,,
	7·2 ,,	,,

The excess of iron took exactly 7·2 c.c. $K_2Cr_2O_7$. So far Mr. Brearley and I agree.

The above was repeated, excepting that 1 grm. soft steel was dissolved in sulphuric acid solution containing the bichromate, thus avoiding the reduction with SO_2 and fulfilling the conditions referred to by Mr. Brearley.

This also took exactly 7·2 c.c., and it corresponds with a ferro-chromium of 13·42 per cent chromium. As I felt that the reducing action referred to by Mr. Brearley might take place if it were given more time, I repeated the above experiment and allowed the soda solution to stand all night. I might say there is no excuse for this in actual practice, because the solution filters remarkably quickly. The bichromate solution taken was 8·4 c.c., equal to a loss of 1·2 c.c., or 0·37 per cent chromium.

The above were repeated and verified by our Mr. Macgregor, who got exactly the same figures.

I think the above fairly dispose of the objections raised by Mr. Brearley, and I think he will find on repeating them, or carrying out similar experiments, that the objection does not apply in the case of a chromium determination.—I am, &c.,

W. GALBRAITH.

C/o Glasgow Iron and Steel Co., Lim.,
Wishaw.

NOTICES OF BOOKS.

An Elementary Treatise on the Metric System of Weights and Measures. By J. HAMBLIN SMITH, M.A. London, New York, and Bombay: Longmans, Green, and Co. 1897. Pp. 103.

IN 1895 a Parliamentary Committee recommended that the metrical system of weights and measures should be at once legalised for all purposes: this was accepted by Parliament, and an Act has been passed to legalise the metric system for the purposes of trade. The Committee also made other recommendations, which, however, were not agreed to. There can be little doubt that the metric system is bound to come in time; in all matters of scientific, *i.e.*, chemical, physical, engineering, &c., calculations, no one would think of using fractions, especially such barbarous fractions as, say, 1 lb. 10 ozs. of mutton at 10½d. a lb.

In the handy volume now before us the author explains and teaches in a most clear and succinct manner the simplicities of the decimal system. A number of problems are set throughout the book, and the correct answers are to be found at the end.

Sugar, Home-grown and Home-manufactured. By SIGMUND STEIN. Liverpool: C. Tinling and Co. 1898. Pp. 71. Illustrated with 19 Engravings.

THE author describes this pamphlet as "a proof that one-and-a-half million tons of sugar consumed annually can be produced at home, and that about £15,000,000 per annum now paid for sugar from abroad can be used to support home industries and save the British farmer from ruin."

The manufacture of beetroot sugar dates from the last century. Marggraf first found that the root contained sugar in 1747, but it was first turned to practical account by Achard some years later, and in the year 1838 there were no fewer than 159 factories at work in different parts of Germany. The French next took the matter up, with the result that at the present day there are nearly 300 beetroot sugar-factories at work in France.

In the year 1853 a factory was started at Mount Mellick, in Queen's County, but it was an utter failure. Another factory was started at Lavenham, in Suffolk, but this failed also. The cause of these disasters is not far to seek, and with proper care and knowledge there is no reason why it should be repeated.

The climate of England is stated by many well-known chemists who have studied the question during the last fifty years to be quite as favourable—if not more so—to the growth of the sugar beet than that of the Continent. Full details are here given as to the necessary character of, and the best method of preparing, the soil intended for growing sugar beet; also detailed instructions as to manuring, sowing, and special cultivation: good cultivators get 14 to 16 tons of roots per acre, giving 12·7 to 16·9 per cent of sugar.

It must be remembered that beetroot takes very large quantities of different plant-foods from the soil, which must of necessity be returned to it; for instance, 100 lbs. of roots and 100 lbs. of leaves take away 43·8 lbs. of nitrogen, magnesia, phosphoric acid, potassium, and lime in varying proportions. The author then gives a lot of figures showing that, under fair conditions, beets can be grown in the United Kingdom at a good profit. Of course a factory must be erected to manufacture the sugar; but Mr. Stein shows (and he has had a great deal of experience) that, on a capital outlay of £60,000, a profit of over 6 per cent can be easily made, taking sugar at the low price of £9 per ton; £12 per ton would give 32 per cent profit.

A good description of the process of manufacturing raw sugar as practised at the present day then follows, with a number of excellent engravings showing the machinery used; the pamphlet closes with a number of tables and statistics concerning foreign factories.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 11, March 14, 1898.

Chemical Actions of the Electric Discharge. Nitro-compounds in the presence of Free Nitrogen.—M. Berthelot.—The principal nitro-compounds experimented on embrace examples taken from the fundamental classes, such as the mono- and poly-amines and the primary, secondary, and tertiary alkalis belonging to the fatty, benzenic, and pyridic series, &c. A large number of results are given, but the paper is far too lengthy for useful abstraction.

Estimation of Carbonic Oxide in Large Quantities of Air.—Armand Gautier.—The author refers to a paper in the last number of the *Comptes Rendus* by M. Nicloux, and claims to have used almost the same method for the past seven or eight years.

Causes of the Reciprocal Displacement of two Acids.—A. Colson.—When a metallic chloride is attacked by a fixed acid, hydrochloric acid gas is given off; while, on the contrary, sulphydric gas is absorbed by pure and dry metallic salts. The first reaction is endothermic, and the second strongly exothermic, but in both cases an increase of temperature assists the reaction, while a lowering of the temperature will retard or even stop it entirely.

New Silicide of Chromium.—Ch. Zettel.—The author has prepared a new silicide of chromium by adding 200 grms. of calcined sesquioxide of chromium to a melted bath of 140 grms. each of copper and aluminium in a fire-clay crucible. On pouring, a metallic ingot is obtained, containing a well-crystallised body, composed of silicon and chromium, having the formula $SiCr_3$. It can be separated from the metals by means of aqua regia. After drying, it is in the form of a grey crystalline powder. Its density at +18° is 6·52. It easily scratches glass, but will not touch quartz; while the silicide obtained by M. Moissan, viz., $SiCr_2$, will scratch even corundum with ease. It is soluble in hydrofluoric acid, but neither hydrochloric or nitric acid or aqua regia have any effect on it. The following figures have been obtained by analysis:—

	I.	II.	III.	Theory for $SiCr_3$.
Si	15·40	—	15·52	15·21
Cr	83·81	84·68	84·98	84·79

New Method of Fractionation of the Yttria Earths.—G. Urbain.—Already inserted in full.

Two Methods for the Decomposition of some Sulphocyanic Ethers.—Œchsner de Coninck.—The author has studied the action of hypochlorites containing an excess of alkali on four sulphocyanic ethers, viz., the sulphocyanates of methyl, ethyl, amyl, and methylene. His results are here described in full.

On some Ether Oxides of β-Naphthol.—F. Bodroux.—Several ether oxides of β-naphthol have been prepared by the action of a fatty bromide or iodide on naphthol-β dissolved in alcoholic potash. The mixture was heated for an hour on a water-bath. As soon as it reached the boiling-point the reaction took place; the colour of the solution changed from green to yellow, while at the same time a white crystalline deposit of bromide or iodide of potassium was formed round the sides of the flask. After cooling, the liquid was decanted and the alcohol driven off by heat; what remained was treated with an excess of potash. The phenolic ether is precipitated and floats on the surface of the liquid; it sometimes solidifies on contact with the air, and can be easily separated.

Sterilisation of Liquids by Filtration.—J. Hausser.—The author has found that of all the substances he has tried for the purification of water by filtration, the infusorial earth called "kieselguhr" has given the best results. It is prepared by first finely sifting, to remove all large particles, and then heating to about 800° or 1000°. On cooling, it must be powdered and levigated to obtain an impalpable powder—though this last operation is only necessary when certain special solutions have to be dealt with, experience alone showing when. To use it, the powder is mixed with a little water and thrown on a filter; as the liquid passes through, the powder remains, and forms a perfect layer for filtration and sterilisation.

Journal fur Praktische Chemie, 1898, No. 2.

β-Naphthoquinolines.—Ad. Claus and H. Besseler.—This substance was prepared by Skraup's method, which gave a good yield when enough concentrated glycerin was used and the temperature favourable (135—145° is the best). After heating the whole on an oil-bath for about four hours, it was poured into ice-cold water and saturated with alkali. The raw product obtained was fractionally distilled; the fraction coming over at 340° consisting chiefly of naphthoquinoline. The base was purified by dissolving it in the least possible amount of sulphuric acid hydrate, and pouring the cold solution into alcohol. The sulphate separated in pale green crystals, and was decomposed with soda, and the base obtained (m. p. 89—90°). The analysis of this salt corresponded to the formula $C_{13}H_9N$. From this base various salts were prepared: β naphthoquinoline, iodmethylate, chlormethylate, bichromate, methylate, and sulphomethylate.

α- or (1)-Naphthoquinolines.—Ad. Claus and P. Imhoff.—This substance is much more difficult to prepare than the β-naphthoquinoline. The authors find that the best method of preparation is to mix equal quantities of naphthylamine and arsenious acid in the finest powder, then add the glycerin, and finally the sulphuric acid hydrate, whilst the vessel is well shaken. The whole is then heated for some time at 100° and still kept well shaken until it becomes a light brown solution. It can then be heated to 150°, when the final decomposition takes place. The end of the reaction is known when a portion of the substance on dilution gives an orange-coloured precipitate with potassium permanganate, and the liquid is not coloured blue. α-Naphthoquinoline is insoluble in water, but soluble in ether, alcohol, benzene, acetic acid, and carbon disulphide. It melts at 51° and boils at 338°; not far above its melting-point it decomposes. The authors also prepared various salts from the free base.

Structural Relation between the two Naphthoquinolines.—Ad. Claus.—This paper is a discussion on the structural formulæ for the naphthoquinolines, and is unsuitable for abstraction.

Para-pseudopropylnaphthenic Acid.—W. Markownikoff.—This acid is prepared from cuminic acid by hydrogenation. Experience proves that twice acting with sodium in boiling amyl alcohol solution is enough, and a product is obtained free from cuminic acid, but many products of incomplete hydrogenation are formed, and these must be got rid of by the action of manganate solution. A substance is obtained of constant melting-point (94—95°) after re-crystallisation from hot alcohol. The substance, on combustion, is found to correspond to the formula $C_{10}H_{18}O_2$. Various salts of the acid are also prepared.

Allylmethyltertiarybutylcarbinol.—Al. Gnedin.—The author investigates the reaction of iodallyl and zinc on the tertiary butylmethylketones, assuming that the reaction is analogous to the syntheses of other unsaturated alcohols of the general formula $C_nH_{2n-1}OH$, according to the equation:—

$$(CH_3)_3C-CO-CH_3 + Zn<^{CH_2-CH=CH_2}_{I} = (CH_3)_3C-C(CH_3)(O(ZnI))-CH_2-CH=CH_2$$

The ketone and iodallyl are dropped on zinc and cooled with ice, and left standing for some time. It can then be worked up with water and distilled; the purest fraction coming over at 165—168°. It is a light yellow mobile liquid with a smell of camphor, solidifying at −7°. This substance can be oxidised to the corresponding glycerin with permanganate; the glycerin being crystallised many times from ether (m. p. 87—88°).

Unsaturated Hydrocarbons.—R. Walther.—When benzylcyanide and benzaldehyd are heated to a temperature above 200°, not only is water split off, but a secondary action takes place: saponifying of the cyanogen group and formation of CO_2. In a similar manner, when benzaldehyd and phenylacetic acid are heated under pressure, stilbene is formed. The temperature of maximum stilbene formation appears to be 250°. On cooling the mixture, the stilbene partially separates out in large crystals. Salicylic aldehyd and cuminic aldehyd react in an analogous way.

Zeitschrift für Physikalische Chemie,
Vol. xxv., No. 1.

Experimental Investigation of the Dissociation of Substances Dissolved in Aqueous Alcohol.—Ernst Cohen.—The substances were examined with regard to their dissociation, both when dissolved in pure alcohol and in aqueous alcohol; the alcohol content varying from 0—100 per cent. The experiments took place at 18°. The salts used were KCl, KI, KCl, NaCl, HCl. As a result of these experiments it was found that—(1) in dilute aqueous alcohol solutions the influence of the alcohol content on the molecular conductivity is independent of the concentration of the solution; (2) the molecular conductivity of an aqueous alcohol solution can be deduced from the equivalent water solution through multiplication by a factor which is constant for each alcohol content.

Employment of Metallic Sulphides as Electrodes.—Isidor Bernfeld.—In the electrical separation of Cu from its ores, the Cu is first washed to free it from all impurities except the noble metals, and is then used as an anode. By this means pure Cu is deposited on the cathode, while the other metals fall to the bottom. Lately it has been suggested that raw galena might be used as anode, but the method has been given up owing to the presence of various impurities in the ore. The author has investigated in this connection the phenomena attending the employment of galena and other metallic sulphides, both as anode and cathode. He finds that as anode in an acid cell the metal goes into solution and sulphur is deposited; with greater current density the S is oxidised. As cathode in an acid cell, H_2S results, and the metal remains behind. As anode in alkaline solution, the metal is changed to hydroxide, and the S oxidised; while as cathode in alkaline solution, alkali sulphide is formed and the metal remains behind.

Dissociation in Mixed Salt Solutions.—A. Fock.—The author shows that, on the assumption that in a mixed solution of two binary electrolytes with a common ion, the degree of dissociation of both salts is not equal, nor equal to that of the entire concentration. His former results on the mixed crystals of ammonium chloride and potassium chloride are in entire conformity with the distribution law and the law of mass action.

Universal Applicability of the Law of Dilution.—J. J. van Laar.—As is well known, the law discovered by Ostwald for weak electrolytes does not hold for substances which, like HCl, are to a great extent dissociated in aqueous solution. The author attempts to explain this by an assumption, which is supported by several arguments, that the electrical conductivity of a good electrolyte is not an exact measure of its degree of dissociation, *e.g.*, assuming that the dilution law does hold, the calculated heat of solution of Aq acetate is 4369 g. cal; of Aq propionate, 3789 g. cal.; and of Aq isobutyrate, 2715 g. cal. Whereas the numbers found by Fr. von Maarseeven were 4613, 3980, and 2860 g. cal. respectively; the error in each case being only about 5 per cent, although the degree of dissociation employed in the calculation is that determined by conductivity. The author believes that the degree of dissociation in a good electrolyte is modified by the passage of the current, in that the temperature of its ions and molecules is much higher than that of the surrounding medium.

Relationship between Heat of Solution, Solubility, and Degree of Dissociation.—Heinrich Goldschmit.—The substances used were silver acetate, silver isobutyrate, silver propionate, and *o*-nitrobenzoic acid. The dissociation was found for saturated solutions at 25°. The heat of solution was measured in a Pt calorimeter, a solution of $AgNO_3$ being first added, and enough of a sodium salt to form the required salt, and the rise of temperature measured. The results of the experiment were compared with the calculated results according to van't Hoff's and van Laar's formulæ. In the case of the silver salts, neither formula gave good results.

Equilibrium between Ammonium Nitrate and Ammonia.—B. Kuriloff.—Ammonium nitrate is only in a position to give a single compound by the absorption of dry ammonia; the composition probably being $NH_4NO_3.3NH_3$, and the range over which this compound can exist lies at a very low temperature—from −40° onwards. At higher temperatures, until we reach the melting-point of ammonium nitrate, there is only the phase, solid ammonium nitrate.

Separation of Helium from a Natural Compound with strong Development of Light and Heat.—Julius Thomsen.—This mineral consists chiefly of fluorspar, but has a small percentage of fluo-compounds of Ce and Yt group. When powdered and heated, light and heat are developed, and it glows with a gold-coloured light. A gas is given off which, by the spectroscope can be recognised as helium.

Passage of Electric Currents in Mixed Solutions of Electrolytes.—K. Hopfgartner.—Mixtures of normal solutions of NaCl and HCl, $BaCl_2$ and HCl, and $MgSO_4$ and $CuSO_4$ were employed for this research. The chlorine was estimated with silver. The experimental results agree very well with the calculated ones, except in two experiments with $MgSO_4$ and $CuSO_4$.

Dissociation of Dibasic Organic Acids. Part I.—W. A. Smith.

MEETINGS FOR THE WEEK.

MONDAY, 25th.—Society of Arts, 8. (Cantor Lectures). "Sources of Commercial Indiarubber," by Dr. D. Morris, C.M.G.

TUESDAY, 26th.—Royal Institution, 3. "Phases of Art—Past and Present," by T. C. Gotch.

WEDNESDAY, 27th.—Society of Arts, 8. "Photography and Colour Printing," by Captain W. de W. Abney, C.B.

THURSDAY, 28th.—Society of Arts, 4.30. "India and Her Currency," by Sir Edward Sassoon, Bart.

—— Royal Institution, 3. "Some Leaders in the Poetic Revival of 1760-1820—Cowper, Burns, and Scott," by The Rev. Canon Ainger, M.A., LL.D.

FRIDAY, 29th.—Royal Institution, 9. "Magneto-optic Rotation and its Explanation by a Gyrostatic Medium" (with Experimental Illustrations), by Professor Andrew Gray, M.A., LL.D., F.R.S.

SATURDAY, 30th.—Royal Institution, 3. "Programme Music" (with Musical Illustrations), by Sir Walter Parratt, Mus. Doc., Master of the Queen's Music.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2005.

NOTE ON A CURIOUS LEAD SALT. THE DOUBLE IODIDE OF LEAD AND POTASSIUM, $PbI_2,2KI$.

By FREDERICK C. HUXLEY BROOKS.

Early in 1897, while testing a sample of zinc shavings for lead, I noticed that the addition of an excess of potassium iodide to a lead salt caused the precipitated iodide to change from an orange-yellow to a white colour. This change I found was due to the formation of a double iodide of potassium and lead. Although discovered nearly a year ago it is only recently that I have had time to investigate the compound fully. The result I am tempted to lay before the chemical world, chiefly on account of the remarkable property the iodide possesses of being decomposed by water, with the formation of iodide of lead (PbI_2) and potassium iodide; thus:—$PbI_2,2KI = PbI_2 + 2KI$. The action of water appears to be catalytic, unless, indeed, the hypothesis be advanced that potassium iodide forms a hydrate which is decomposed when its solution is evaporated; in which case:—

$$PbI_2,2KI + xH_2O = PbI_2 + KI,xH_2O.$$

This peculiar property makes the iodide a most delicate test for water. I have often detected the presence of moisture in chloroform and ether when anhydrous copper sulphate failed to show the least change of colour.

Preparation.—One grm. of lead nitrate is dissolved in 10 c.c. of distilled water. A saturated solution of potassium iodide is then added until the precipitate is just dissolved. The solution is allowed to stand for a few minutes, when a copious crystalline precipitate of the double iodide falls. The supernatant liquor is quickly poured off (and preserved), and the precipitate shaken for a few minutes with about 10 c.c. of absolute alcohol. This removes any excess of KI from the double iodide, the latter being insoluble in alcohol. The alcohol is then poured off, and the salt quickly dried with filtering paper. It should be preserved in a stoppered bottle over calcium chloride.

The salt occurs in silky acicular crystals of an almost white colour. So easily is it affected by moisture that, when exposed to the air of a room for a few minutes, it begins to decompose. This is evidenced by it losing its almost white colour and becoming distinctly yellow. When gently heated it also becomes yellow, but it resumes its original colour on cooling. Heated more strongly it is partially decomposed, iodine vapours appearing.

The salt is very slightly soluble in boiling chloroform, but is easily dissolved by a strong solution of iodide of potassium. The mother-liquor from which the double iodide has been obtained holds a certain further amount in solution. This can be recovered by adding 1 c.c. or less of lead nitrate solution (10 per cent), stirring until the PbI_2 is dissolved, and allowing the precipitate to form. The solution can then be decanted from the precipitate and treated again as before, until the iodide is all precipitated and the excess of potassium iodide exhausted.

When the saturated solution is left for twenty-four hours in a cool place there is sometimes a considerable deposit of iodide, which then takes the form of very fine acicular crystals of great length (15 m.m.).

It is worthy of notice that, while pure water decomposes the compound, a strong solution of potassium iodide dissolves it.

Composition.—The mean of three analyses gave—

	Calculated to $PbI_2,2KI$.	Found.
PbI	57·963	57·855
KI	42·037	42·145
	100·000	100·000

(The KI was estimated by difference).

The composition is therefore $PbI_2,2KI$.

Charters Towers Mining Institute,
Charters Towers,
Queensland, Australia.

ON THE DECOMPOSITION OF CONCENTRATED SULPHURIC ACID BY MERCURY AT ORDINARY TEMPERATURES.

By CHARLES BASKERVILLE and F. W. MILLER.

In a recent number of the *Journal of the American Chemical Society* (xx., p. 100) Mr. J. R. Pitman denied the statement of the authors that concentrated sulphuric acid is decomposed by mercury at the ordinary atmospheric temperature, 20° C. Mr. Pitman leaves himself open to the same criticism that could with justice be urged against us, namely, failure to report the *strength* of the acid obtained in any other way than that by specific gravity.

As is well known, sulphuric acid 1·84 sp. gr. may contain either 95·6 or 99·2 per cent H_2SO_4. The apparatus at our command does not permit a determination of the specific gravity more accurately than the second decimal place. Sulphuric acid sp. gr. 1·839 contains 99·70 per cent H_2SO_4. The acid used by us in the experiments reported (*vide supra*) contained 99·65 per cent H_2SO_4 by analysis. Acid of that strength placed in an air-tight glass-stoppered bottle with pure mercury gave off in twenty-four hours sufficient sulphur dioxide to bleach a very dilute potassium permanganate solution. In several instances, after allowing a longer exposure, the gas was easily recognised by its odour when the stopper was removed.

Whether or no any reaction occurs depends entirely upon the *strength* of the acid used, as independently noted later by M. Berthelot, who states that "boiled sulphuric acid has a slow action on mercury, forming sulphate and giving off sulphurous acid." He also states that the reaction occurs only at the maximum concentration (Chemical News, lxxvi., 325; *Comptes Rendus*, cxxv., No. 20). When our paper was read before the Society in Detroit, Dr. E. W. Morley, in the discussion following, stated that he had previously made similar observations, but had not published them. In a recent letter from him he stated that, when freshly distilled cold sulphuric acid was in contact with mercury, he found it impossible to maintain a vacuum on account of the evolution of from 1 to 2 c.c. sulphur dioxide per day.

An ordinary hydrometer may indicate 1·84 acid, when in fact it may be 1·837 sp. gr., or 94·2 per cent acid, which fact we have observed. We have lately (since the appearance of Mr. Pitman's paper) observed that 95 per cent acid does not seem to react in the cold with mercury. Further, we have seen that during three weeks in this climate 95 per cent acid dropped to 94·2 per cent by allowing the bottle to remain open a few minutes each day. The content of acid more or less exposed to the moisture of the air while being used in nitrometers could easily change—the stronger the acid the more rapid the change. Acid of 94 per cent serves very well for desiccation in ordinary gas analysis, and has no apparent action upon the mercury; however, the authors insist that

concentrated sulphuric acid of 99·5 per cent strength is decomposed by mercury.

University of North Carolina.

METALLURGICAL NOTES.

Wilborgh's Thermophones.—Ferrosodium.—Manganese Bronze.

By SERGIUS KERN, M.E., St. Petersburg.

1. The very handy thermophones of Prof. Wiborgh, of Stockholm, are in constant use at the Baltic Works for several purposes:—For measuring the heat in chimney flues; under the boilers; for taking the temperature of copper alloys before casting; for the same purpose, in connection with the small Bessemer for steel castings.

The thermophones, as many perhaps know, consist of cylinders of fire-resisting material, containing inside a fulminating compound, and represent a simple method for approximative estimation of heats in metallurgical operations, quite good enough for ordinary purposes.

For instance, the cylinder is thrown into a ladle of cast-iron ready to be poured into the converter; long before the ladle is brought up to the mouth of the vessel, the cylinder explodes. The time in seconds is noted, and in the tables attached to every box (50 thermophones) the temperature may be read. Sometimes, through a fault, the cylinders do not explode. We make another trial. In some instances we throw two thermophones at once, and take the mean number of seconds elapsed before the explosion.

We have used these thermophones for more than a year at the above-named works in the steel foundry, and have certainly found a great advantage in knowing the temperature of cast-iron run out of the cupola for the small Bessemer; next we know, at intervals and at the end, the temperature of the liquid metal in the converter itself: we turn the vessel for a few seconds, and measure the heat by throwing in a cylinder.

By such means we easily know what must be done with the metal, and for what castings, big or small, the steel is good.

The average temperature of cast-iron before pouring into the converter is 1400° to 1500° C. But in cold runs of the cupola the temperature comes down to 1000°. When ready the steel is at 2200° to 2400°, and often higher: these higher temperatures cannot be estimated by the described method.

We have ascertained the temperature of crucible steel prepared in our naphtha-fired furnaces; the temperature just before pouring, for steel castings also, is 2200°. Such experiments prove that naphtha-burning furnaces for melting steel are far more convenient in comparison with the coke furnaces, and nearly equal to the Siemens gas-crucible furnace; but are more cheap and handy than the latter when small quantities of steel are melted at a time—say 3 cwts. Morgan's crucibles are used by us; they stand well several heats. But, strange to say, there is not a single works here making crucibles for the market. Several big Russian steel establishments make crucibles, but for their own use only.

2. I had an opportunity to experiment myself, and to witness some others try the ferrosodium supplied by Mr. Blackwell, of Liverpool. In crucible steel this reducing flux makes the slags thinner, but aluminium had still to be used. But in casting a steam cylinder jacket, some 4 tons in weight, there was a visible improvement. The charge in the cupola contained 75 per cent of machine scrap and 25 per cent of pig-iron. The ferrosodium was thrown into the ladle, and gave, when the cast-iron was poured into it, dense fumes. The regulations, here, prescribe 2000 English lbs. as breaking load for test-pieces (1 inch × 1 inch and 12 inches long); the cast-iron treated with the ferrosodium gave, as breaking-strain, 2200 and 2800 lbs. The alloy cleans the metal in the ladle. A firm in the south of Russia gives me the same account.

3. I am working with the assistance of the laboratory of the Obouchoff Works, near St. Petersburg, on bronze alloys, produced by the addition of Mr. Keiffenheim's "special manganese alloy." Properly brasses are made, but they have the qualities of bronzes, without using expensive tin in the charge. The preliminary experiments gave the following results:—

Breaking strain.	Elongation (per cent).
26·4 tons per sq. inch.	24·9 in 8 inch.
22 „ „	15·4 „

The second test showed the metal imperfectly mixed. A description of further experiments shall follow.

St. Petersburg, New Admiralty.

NOTE ON SOME REMARKABLE THERMO-EFFECTS PRODUCED UNDER THE INFLUENCE OF HIGH PRESSURE.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

The apparatus made use of, in order to conduct these investigations, consisted in a small platinum tube 1/16th of an inch in diameter by ¼ inch thick, this being enclosed in a further tube constructed of cold-drawn steel, 12 inches in diameter and 2 feet long, an interior perforation having been made in it presenting a diameter of ½ an inch and extending to a depth of 6 inches. The steel jacket itself was furnished with a specially cut thread of 3 inches deep, and mounted with a formidable steel cap, corresponding in thickness and diameter to the bottom of the steel tube, and in length measuring from the extremity of the central excavation, whilst the cap real was also drilled through the top, in order to allow of the insertion of a suitable lever when desirous of examining the internal contents.

In the first experiment 1 inch of the platinum tube was filled with distilled water, the further end being hermetically sealed by means of the oxygen blowpipe, and tightly packed with fine magnesia previous to confining it by screwing on the steel cap. The jacket and its contents were now slowly raised to a full red heat and maintained for three hours at that temperature; then taken from the furnace and allowed to cool, the cap unscrewed, and the platinum point removed, the quantity of water recovered being about three-fourths of the original quantity inserted. The most curious observation of this remarkable experiment was the powerful odour of ozone perceptible, as well as the presence of small quantities of hydrogen peroxide, both of which the remaining aqueous portion proved upon examination to be impregnated at the same time with substances one would least have expected to find under such circumstances.

In the second series of experiments the temperature was urged to whiteness; upon examination being made, the entire contents of the platinum tube had disappeared, leaving the platinum surface comparatively unaffected, whilst that portion of the magnesia lining in closest proximity to the platinum had become somewhat crystalline.

In the third series of experiments 5 grains of cane-sugar were enclosed, and treated at a red heat for five hours, the contents upon examination amounting to a few drops of water, accompanied by a powerful odour of acetylene, as well as the production of an extremely hard and crystalline graphite, presenting when microscopically examined an appearance closely resembling the best cut

retort carbon, with a corresponding brilliancy to that of crystalline silicon.

In the last series of experiments, the author being anxious to ascertain the electrothermic results obtainable by the enormous pressure thus exerted, the steel cap of the apparatus had accordingly to be somewhat altered, in order to insulate an inserted platinum wire; accordingly, a perforation having been made through the cap of the apparatus to allow of this being done, 3 c.c. of distilled water were next introduced into the steel jacket itself, and a platinum wire of No. 10 gauge inserted through the small opening, insulated by means of asbestos fibre, and luted as well as possible to the steel. The entire apparatus was now raised again to a dull red heat, whereupon—the projection wire having been brought within close proximity to the steel case—vivid sparks, 1/16th of an inch in length, formed a continuous discharge, which gradually increased in length, but unfortunately came to an abrupt termination by the lifting of the sealed joint, which naturally presents insurmountable difficulties in order to obtain anything like a true closure; further experiments are, however, being contemplated which it is hoped may bring to the front some important changes both in chemical and electrical matters; but the terribly dangerous nature of the experiments, and consequently the great care required when conducting the same, to a great extend retards, in many instances, what otherwise might blossom into valuable results.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

ON NEODYMIUM.

By O. BOUDOUARD.

In the year 1885 M. Auer von Welsbach described a method for the separation of lanthanum and didymium, and also for the subdivision of didymium into praseo- and neodymium: this method depends on the difference in solubility, in dilute nitric acid, of the double nitrates of didymium and ammonia, and of lanthanum and ammonia.

In following up my researches on the yttric earths, I have always endeavoured to obtain the earths in as perfect a state of purity as possible. To separate these earths from those of the ceric group, which may possibly be present, the best method is to use sulphate of potassium; the earths of the ceric group give a double sulphate, insoluble in a saturated solution of an alkaline sulphate; those of the yttric group give a soluble double sulphate.

Preliminary trials enabled me to isolate a very small quantity of an oxide having an atomic weight of 142·7, of which the salts gave the absorption spectrum of neodymium, such as was described by M. Auer von Welsbach. This oxide was obtained in the following manner:—The yttric oxides, which had already been purified, were converted into sulphates, and the aqueous solution of these sulphates was treated with an excess of sulphate of potassium; this is left for about twenty-four hours, and the double sulphate formed is collected on a filter, then decomposed by hot soda. The oxide, after being completely freed from alkali, is dissolved in nitric acid, and then precipitated by oxalic acid.

I was anxious to see if a fresh experiment would confirm these results. For this purpose 70 grms. of yttric oxides were submitted to the same treatment as just described, and I was thus able to isolate a certain quantity of an oxide of which the solution gave the spectrum of neodymium. After having removed the thorium, by the formation of the double sulphate of neodymium and sodium, insoluble in a saturated solution of sulphate of sodium, I analysed the product finally obtained. The results were as follows:—

Anhydrous sulphate used ..	2·758 grms.
Oxide obtained	1·605 ,,

This gives as atomic weight for the corresponding metal the figure 143.

The oxide obtained after calcination is of a greenish colour; the oxalate and the anhydrous sulphate have a slightly rose-coloured tint. The crystallised sulphate is rose-coloured, and is less soluble in water than the anhydrous salt; this solubility is more marked in the cold than when the solvent is hot; these properties relative to solubility are characteristic of all the rare earths.

The absorption spectrum of the solution of the sulphate is characterised by the following wave-lengths:—

591·5 to 584	Vague.
584 ,, 572	Very strong.
523 ,, 519	Strong.
512 ,, 508	Faint.
480	Very faint.
470	Very faint.

I was able to compare this spectrum with that of a solution of neodymium belonging to the laboratory, and thus assured myself of their identity; the very faint lines (480 and 470) are very likely due to traces of praseodymium.

The conclusions to be drawn from the above facts are that neodymium gives a double sulphate with potassium, more soluble than that of praseodymium, which enables us to make a more rapid separation than is perhaps possible by fractional crystallisation. I intend applying this method, founded on the relative solubilities of the double alkaline sulphates, to the study of the didymium salts. —*Comptes Rendus*, vol. cxxvi., No. 12.

ON THE YTTRIC EARTHS CONTAINED IN THE MONAZITE SANDS.*

By P. SCHÜTZENBERGER and O. BOUDOUARD.

For the last three years I (O. B.) have been working on the yttria earths. I commenced this work under my esteemed master the late P. Schützenberger, who did not hesitate to collaborate with me, in face of the difficulty of the question (*Comptes Rendus*, cxxii., p. 697; cxxii., p. 782). It is the results which we obtained that form the subject of this memoir.

By *yttric earths* we mean all the earths giving double potassic sulphates soluble in a saturated solution of an alkaline sulphate, but precipitated by oxalic acid and oxalate of ammonia; this last reagent not being employed in excess. The proportion contained in the monazite sand that we had at our disposal was unfortunately small, so that we were obliged to use several kilogrms. of the mineral in order to obtain a sufficient quantity of the oxides.

Extraction of Yttric Earths.—The mother-liquors of the double sulphates are precipitated hot by potash. After washing with warm water, the oxides are dissolved in nitric acid, and re-precipitated by ammonia. This treatment is repeated several times, so as to make quite certain that all traces of alkali have been eliminated; this precaution is indispensable for certifying to the correctness of the figures obtained after the calcination of the sulphates. Finally, the oxides are dissolved in nitric acid and precipitated by oxalic acid. The oxalate is washed by decantation and filtration, then dried and calcined to obtain the oxide, which exists as a yellow powder easily soluble in mineral acids.

Method of Fractional Crystallisations.— The yttric oxides are dissolved in nitric acid, and the nitrate converted into sulphate. The sulphate is gently calcined so

* *Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 6.

as to drive off the excess of sulphuric acid; after this dehydration and cooling, it is taken up by cold water. This solution must be heated on a water-bath; we then obtain a crust of rose-coloured crystals, which are collected. When there is a sufficient deposit, the mother-liquor is decanted and a further evaporation started. This must be repeated time after time, and we thus obtain a series of fractional crystallisations which have been successively analysed:—

First Crystallisation.

Water of crystallisation .. .. 21·95 per cent
Hydrated sulphate used .. .. 4·9884
Anhydrous sulphate obtained.. 3·8931

Atomic weight .. .. 105·9
Anhydrous sulphate used .. 1·8848
Oxide obtained .. .. 0·9798

Second Crystallisation.

Water of crystallisation .. .. 21·92 per cent
Hydrated sulphate used .. .. 5·1254
Anhydrous sulphate obtained.. 4·0015

Atomic weight .. .. 105·75
Anhydrous sulphate used .. 1·9967
Oxide obtained .. .. 1·0374

Third Crystallisation.

Water of crystallisation .. .. 21·98 per cent
Hydrated sulphate used .. .. 10·4708
Anhydrous sulphate obtained.. 8·1739

Atomic weight .. .. 104·6
Anhydrous sulphate used .. 1·7912
Oxide obtained .. .. 0·9266

Fourth Crystallisation.

Water of crystallisation .. .. 21·71 per cent
Hydrated sulphate used .. .. 7·9209
Anhydrous sulphate obtained.. 6 1999

Atomic weight .. .. 100·6
Anhydrous sulphate used .. 2·0310
Oxide obtained .. .. 1·0347

Fifth Crystallisation.

Atomic weight 100 2
Anhydrous sulphate used .. 1·4926
Oxide obtained 0 7593

The three first crystallisations (105·9, 105·75, 104·6) were added together and then submitted to a fresh fractionation in four parts. This gave the following results:—

First Crystallisation.

Water of crystallisation .. .. 21·80 per cent
Hydrated sulphate used .. .. 6·4190
Anhydrous sulphate obtained.. 5 0195

Atomic weight .. .. 106·3
Anhydrous sulphate used .. 1·9109
Oxide obtained .. .. 0·9949

Second Crystallisation.

Water of crystallisation .. .. 21·98 per cent
Hydrated sulphate used .. .. 9·9875
Anhydrous sulphate obtained.. 7·7907

Atomic weight .. .. 105·2
Anhydrous sulphate used .. 1·7465
Oxide obtained .. .. 0·9053

Third Crystallisation.

Water of crystallisation .. .. 22·30 per cent
Hydrated sulphate used .. .. 2·4220
Anhydrous sulphate obtained.. 1·8917

Atomic weight .. .. 101·1
Anhydrous sulphate used .. 1·8897
Oxide obtained .. .. 0·9649

Fourth Crystallisation.

Atomic weight .. .. 100·1
Anhydrous sulphate used .. 0·9041
Oxide obtained .. .. 0·4598

These two series of results show most conclusively that we have to deal, not with one earth only, but with a mixture of earths. The variations in the figures obtained in the determinations of the atomic weights are a sufficient proof of this.

We shall not in future give more than the series of results which appear to be of the most interest.

The sulphates which gave 106·3 and 105·2 as atomic weights were mixed and submitted to a fresh fractional crystallisation:—

First Crystallisation.

Water of crystallisation .. .. 21·79 per cent
Hydrated sulphate used .. .. 4·5412
Anhydrous sulphate obtained.. 3·5519

Atomic weight .. .. 109·25
Anhydrous sulphate used .. 2·0993
Oxide obtained .. .. 1·1067

Second Crystallisation.

Water of crystallisation .. .. 21·80 per cent
Hydrated sulphate used .. .. 8·2052
Anhydrous sulphate obtained.. 6·4519

Atomic weight .. .. 108·75
Anhydrous sulphate used .. 1·9510
Oxide obtained .. .. 1·0247

Third Crystallisation.

Water of crystallisation .. .. 21·90 per cent
Hydrated sulphate used .. .. 10·8672
Anhydrous sulphate obtained.. 8·4847

Atomic weight .. .. 106·2
Anhydrous sulphate used .. 2·1320
Oxide obtained .. .. 1·1094

Fourth Crystallisation.

Atomic weight .. .. 97·3
Anhydrous sulphate used .. 1·1233
Oxide obtained .. .. 0·5648

The two first crystallisations having given 109·25 and 108·75, were mixed and submitted to a further fractionation:—

First Crystallisation.

Water of crystallisation .. .. 21·57 per cent
Hydrated sulphate used .. .. 8·0642
Anhydrous sulphate obtained.. 6·3244

Atomic weight .. .. 109·3
Anhydrous sulphate used .. 2·0611
Oxide obtained .. .. 1·0849

Second Crystallisation.

Water of crystallisation .. .. 22·01 per cent
Hydrated sulphate used .. .. 4·4826
Anhydrous sulphate obtained.. 3·4953

Atomic weight .. .. 105·0
Anhydrous sulphate used .. 2·1441
Oxide obtained .. .. 1·1107

The sulphate 109·3 was, in its turn, fractionated:—

First Crystallisation.

Water of crystallisation .. .. 21·34 per cent
Hydrated sulphate used .. .. 4·4474
Anhydrous sulphate obtained.. 3·4985

Atomic weight .. .. 111·3
Anhydrous sulphate used .. 1·7942
Oxide obtained .. .. 0·9510

Second Crystallisation.

Water of crystallisation	21·97 per cent
Hydrated sulphate used	3·4944
Anhydrous sulphate obtained..	2·7266
Atomic weight	107·2
Anhydrous sulphate used ..	1·4702
Oxide obtained	0·7680

The sulphate 97·3 obtained by a preceding operation was fractionated again:—

First Crystallisation.

Water of crystallisation	21·83 per cent
Hydrated sulphate used	2·9693
Anhydrous sulphate obtained..	2·3210
Atomic weight	100·7
Anhydrous sulphate used ..	2·3192
Oxide obtained	1·1821

Second Crystallisation.

Water of crystallisation	21·78 per cent
Hydrated sulphate used	1·5190
Anhydrous sulphate obtained..	1·1881
Atomic weight	93·9
Anhydrous sulphate used ..	1·1776
Oxide obtained	0·5838

(To be continued).

THE DIGNITY OF ANALYTICAL WORK.*

By C. B. DUDLEY.

(Concluded from p. 187).

PERHAPS I may venture to give you still one more illustration of how, in the course of analytical work, new and apparently hitherto unnoticed reactions may be hit upon, and modifications of methods result. Every chemist who has done much work in determining phosphorus in iron or steel, by the reduction of the molybdic acid of the yellow ammonium phosphomolybate, and subsequent titration of the reduced solution, cannot fail to have been annoyed by the occasional failure of duplicates to agree. Apparently in the two analyses everything has been done exactly alike, and yet the results do not agree. Every thoughtful chemist cannot fail to have felt at such times that somewhere in the method there were conditions affecting the result that were not fully controlled. During the last six or eight months in our laboratory we have apparently struck one of these hitherto uncontrolled conditions, whose influence is not large, and yet enough to at times cause annoying discrepancies in duplicates, or between different chemists working on the same sample.

In order to make clear what follows it should be stated that, in the ordinary working of this method, the yellow precipitate, after careful washing, is dissolved in ammonia, and this solution then treated with sulphuric acid largely in excess, and diluted to a definite volume, in which condition it is passed through the reductor, and subsequently titrated with standard potassium permanganate. The reductor in common use consists, as is well known, of a tube of heavy glass, about 5/8ths of an inch internal diameter and about a foot long, filled with powdered zinc, the top being fitted with a funnel and the bottom with a stopcock. Below the stopcock a smaller tube carries the rubber cork, by means of which the reductor is fitted to the flask which receives the reduced solution. This smaller tube usually projects into the flask an inch or two, and it is customary to use the pump to draw the liquid through the reductor. This much being premised, we may say that in a communication from Mr. Porter W. Shimer, one of the members of the Sub-committee on Methods of the Committee on International Standards for the Analysis of Iron and Steel, he, among other things, called attention to the fact that when making a number of determinations on the same sample, all other things being the same, he got a reduced solution that required more permanganate if he prolonged the small tube below the stopcock in the reductor, nearly to the bottom of the flask, than if this small tube projected only an inch or two into the flask. This statement brought afresh to our minds a thought that every one who has worked much with molybdic acid must have had, viz., that reduced molybdic acid is very easily re-oxidised. We accordingly determined to find out, if possible, whether this was actually the case, and, if so, how much this difficulty might amount to. Accordingly, a stock solution of ammonium molybdate dissolved in water was prepared, and a number of aliquot parts of this solution measured out. Now, obviously, there are two chances for the reduced solution to become oxidised by exposure to the air. One of these is from the air in the flask during the reduction, and on the other from the outside air during the titration. Without going into minute detail, it is perhaps sufficient to say that when we reduced an aliquot part of our stock solution, using the short tube of the reductor, and adding the permanganate drop by drop, with continual agitation during the whole titration, we used 22·7 c.c. of our standard permanganate, all figures given being a mean of a number of closely agreeing determinations. When now we made the reduction the same as before, viz., with the short tube of the reductor, but titrated by allowing about 95 per cent of the permanganate required to run into the flask before agitation at all, and finishing the titration drop by drop, we used 23·1 c.c. of permanganate; in other words, so sensitive is a reduced solution of molybdic acid, that it is easy by varying the mode of titration to introduce considerable error. Prolonging now the tube at the bottom of the reductor as suggested by Shimer, which would result, as is apparent, in a diminished exposure of the reduced solution to the air in the flask before titration, we found our aliquot part to use up 23·6 c.c. of permanganate. But even with the prolonged tube there is some exposure of the reduced solution to the air during the reduction. Accordingly, on the suggestion of my principal assistant, Mr. F. N. Pease, we put a measured amount of standard permanganate solution into the flask which was to receive the reduced solution, more than sufficient to react with it, and then prolonged the tube from the reductor, to dip below the surface of this permanganate. Obviously with this arrangement the reduced solution is entirely prevented from air exposure. On making the reduction and titrating the excess of permanganate with standard solution of ferrous sulphate, it was found that the aliquot part had now used up 24·1 c.c. of permanganate,—an extreme difference in amount of permanganate used, under the varying conditions described, of nearly 6 per cent. Obviously, if two chemists were working on the same sample of molybdic acid, one employing the manipulation first described, and the other that last described, the discrepancy between them would be serious. The discrepancy on phosphorus in steel, while the same in percentage, is very much smaller in actual figures, but still enough to be annoying. The work above referred to is not yet quite finished, but enough has already been done to demonstrate that the ordinary method of determining phosphorus in steel can be advantageously modified in the interests of greater accuracy; and also, although not yet rigorously demonstrated, there are strong indications that molybdic acid (MoO_3) is always reduced by zinc to Mo_2O_3, and that the more complex formulæ, $Mo_{12}O_{19}$, $Mo_{24}O_{37}$, &c., so commonly given as representing this reduction, simply mean that the conditions under which these formulæ were obtained permitted the re-oxidation of the reduced solution to the extent indicated.

* Presidential Address delivered at the Washington Meeting of the American Chemical Society, December 29, 1897. From the *Journal of the American Chemical Society*, vol. xx., No. 2.

There is another phase of this question we are discussing, "The Dignity of Analytical Work," which will perhaps bear a few words. It seems to be universally conceded that the brain that plans and guides is worthy of more honour than the hand that executes; the general deserves more than the private soldier; the architect, than the builder; the investigator who plans the work, than the chemist who makes the analyses. Few will object to such a distribution of rewards as this, and certainly no one will claim that a chemist who, machine-like, simply follows directions, without thought or interest in the matter, can fairly claim recognition for anything more, perhaps, than manipulative skill and honesty. But, on the other hand, is it fair to say that such analysts can truly be called analytical chemists? Does not the genuine analytical chemist embody within himself, not only the capacity of brain to wisely plan his method of attack, to conceive which one of the possible reactions in the case it will be best to employ, but also the requisite manipulative skill to carry out the line of action decided upon? To my mind these two things—viz., the brain power necessary to plan the work, together with the continual activity of the brain while the work is going on, and the skilled and trained hand requisite to do the work—are necessarily coexistent at the same time in the good analytical chemist, and woe be that chemist who tries to put them asunder. The analyst whom chance or the exigencies of earning his livelihood have thrown into a situation, where day after day he must, for a time at least, do the same thing over and over again, and who does not, even in this situation, use his brain constantly, does not each time he adds a reagent think what is going on in the beaker, does not each time he washes a precipitate think what he is washing out, does not every time he makes a weight take a genuine interest in the result, and even the hundredth time that he makes the same determination, is not on the look-out for some flaw in the method he is using, or some possible new reaction in connection with it; such an analyst I say will stand a good chance to remain a routine chemist all his life.

On the other hand, what shall we say of those chemists who plan out a line of investigation, and are content not to make the necessary analyses themselves? We are quite well aware that at the present time this is a very common method of making investigations, and we can, of course, understand that pressure of other duties may make it impossible to pursue investigations in any other way. But we cannot regard this state of affairs as, to say the least, anything less than unfortunate. If we may trust our own experience, the time spent in making the analyses required by one line of attack on a stubborn problem is most valuable, in the opportunity which it affords for carrying the problem in mind, and planning out other lines in case the one in hand does not succeed. Moreover, still more valuable is it to make the analyses yourself, in that while doing so you so frequently get suggestions from the work that are the very ones upon which final success depends. I wish there was time to illustrate this point as its importance deserves, but the history of chemistry and your own experience will have to furnish them to you. To our minds it is hard to overestimate the importance, especially to a young investigator, of his doing his own analytical work for himself. If we read rightly, this was the almost universal habit of the old masters of our science, and we greatly fear that those chemists who from choice delegate their analytical work will find, after years of such delegation, that their reward of successful investigations is very small.

A single thought farther. At the present time so much applied chemistry is either based on analytical work, or has analytical work as an almost essential constituent of its existence, that in a paper discussing analytical work a few words may not be amiss on the relations between pure and applied chemistry. Without wishing to touch in the slightest degree on mooted or disputed questions, it may not be unfair to say that while the applied chemistry does truly, as the name indicates, in the mass of his work, utilise or apply the discoveries of others to useful effect, it does not at all follow that in the field of applied chemistry no discoveries yet remain to be made. It is certainly not too much to say that no thoughtful chemist has ever worked for any length of time in any field of applied chemistry without finding himself surrounded with problems involving new and unknown reactions, with problems—am I not safe in saying—requiring for their solution as good appliances, as deep study, and as keen thought, as any that occupy the minds of the pure chemists. These problems continually force themselves upon him, and his only regret in the matter is that the time at his disposal does not permit him to solve them as fast as they arise. A prominent feature of these applied chemistry problems remains to be mentioned, viz., they generally have immediate useful applications as soon as they are solved. The applied chemist usually makes an excursion into the unknown, because some difficulty has arisen in the course of his regular work, or because some new, more rapid, or more economical method of accomplishing results is desired. He may succeed in finding a new reaction, or in utilising an old one, as the basis of a successful commercial process, or in modifying a manufacturing method in the interests of both economy and speed. But whatever his work, the immediate useful application of the information he secures is both his stimulus and guide. He may not be able, from lack of time, to follow his work up, and find the complete relations of the facts ascertained to the other branches of chemistry, but this is his misfortune rather than his fault, and this condition of affairs, viz., being unable to follow out to completion lines of research one started on, is, if we understand the matter rightly, not characteristic of the applied chemist alone. This much being said, let us ask in what respects the pure chemists resemble or differ from those who work in the field of applied chemistry. They certainly are alike in this, that neither of them can devote his whole time to original work. Both must devote no small portion of their energy to other lines than making investigations. There may have been a time in the history of chemistry when investigators were so fortunately situated that they could devote their whole time and energy to finding out new truth, and giving their results to the world. All honour to such investigators. Moreover, we all know that occasionally an appropriation of funds or an endowment is made for research in some special field. But truly would it not be too much to say that the work of any large percentage of the pure chemists of to-day is the result of such fortunate circumstances? Furthermore, the pure and applied chemists are alike in that, in their original work, both are seeking for the truth, and, if they are successful, both are adding to the sum of human knowledge. They differ, as it seems to me, principally in this:—First, the researches of the applied chemists being largely made in the interests of corporations or manufacturing establishments, the results of these investigations, in many cases, are not at once available to the world, except in so far as they lead to diminished cost of production. Those who have paid for these researches naturally feel that they should be allowed a period of time at least to recoup themselves for their expenditures, and so they protect themselves either by patents or secrecy. But this is only a knowledge of the truth deferred. Sooner or later the results of the investigations of all applied chemists are added to the great body of accumulated chemical knowledge. The pure chemist, on the other hand, at once gives the results of his investigations to the world, and is quite content if the publication of his researches shall bring him, as his reward, a modicum of appreciation from his fellows. Second, in their original work the pure chemists differ from the applied chemists in the ulterior purpose for which the investigation is undertaken. As has already been stated, the applied chemist usually undertakes an investigation, tries to find new truth, with the avowed purpose of at

once utilising this truth as soon as it is found. Not so the pure chemists. The problems which they attack and solve so successfully have no necessary relation to subsequent utility. The truth which they discover, and put on record, may be found to be useful at some time, but its possible immediate utility or non-utility is not taken into consideration by the pure chemist, either in his choice of a subject for investigation or in the prosecution of his work. The truth for the truth's own sake is his motto and guiding star.

If we have diagnosed the case correctly, then the principal differences between the pure and applied chemist are that the latter withholds the results of his work from the world for a period of time, while the former gives his at once, and that the latter is, in his original work, seeking for truth that is at once useful as soon as it is worked out, while the former neither knows nor cares whether the truth that he discovers is either now or at any future time turned to practical or useful effect. Let me not be misunderstood. I am not attempting to belittle in any sense the work of the pure chemists. They are worthy of all honour and respect. But, on the other hand, I am not at all willing to have the work of the applied chemists made light of or treated as though it were in an inferior field. To my mind there is no occasion for either to belittle the work of the other. The field of chemistry is so broad, the amount of unoccupied ground in every branch of the science is so great, that there is neither time nor energy for struggling as to who is greatest or who is least; but in whatever line a man's tastes, opportunities, or the force of circumstances may lead him, whether as a pure or an applied chemist, whether organic or inorganic, whether theoretical, physical, or agricultural, whether analytical or synthetic, provided in his mind at all times the love of the truth is above all, and honest work is being done, he is worthy of recognition, honour, and respect.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 21st, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. H. C. Seabrooke, W. W. Cheadle, T. H. Hills, and B. S. Bull, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edwin Dowzard, 30, The Willows, Liverpool; Alexander Grant Russell Foulerton, Dunsdale, Mulgrave Road, Sutton; Oswald Hamilton, Old Stratford, Stony Stratford; George Arthur Jarvis, 66, Millbank, Wellington, Salop; Harry Lancelot Lee, 8, Chichester Street, St. George's Square, S.W.; William Lewins, 43, Exeter Street, Gateshead; Alexander MacGillivray Neilson, Coimbatore, Madras; Henry Trench Waller, Zeehan, Tasmania; Edmund Thomas Whitaker, Swan Hill Court, Shrewsbury; William Ernest Wild, 230, Turton Road, Bromley Cross, near Bolton.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected Fellows of the Society:—

Henry William Coupe-Annable; Albert Abbott, B.A.; Charles Baskerville, B.S., Ph.D.; Joseph Brierley, B.Sc.; Alfred Campion; Robert Martin Caven, B.Sc; Frederick Hudson-Cox; Charles Benjamin Dudley, Ph.D.; John Arnold Fleming; Arthur L. Harry Garside, B.Sc.; William Thomas Gidden; Alexander Guthrie, B.Sc.; John Heaton; Lawrence Hislop; Harry Pearson Hodgson; J. Shearson Hyland, Ph.D., M.A.; Edwin Charles Jee, B.Sc.; Samuel Morton Jessop; Edward Jones, B.Sc.; Thomas Martin Lowry, B.Sc.; George Henry Masson, B.Sc.; Albert Henry Mitchell, B.Sc.; Alfred James Parker; Walter Charles Cross Pakes; Walter Ratcliffe; Francis Pitt Smith; Thomas de Smith, B.A.; Henry Somerville, B.Sc.; William T. Newton Spivey, M.A.; Harry St. John; Samuel Walker, M.A., B.Sc.; John Alexander Williamson; Thomas Barlow Wood, M.A.; Samuel Allinson Woodhead, B.Sc.

Of the following papers those marked * were read:—

*49. "*The Carbohydrates of Barley Straw.*" By C. F. Cross, E. J. Bevan, and Claude Smith.

The authors have continued their investigations of growing barley, extending their observations to the plant under the artificial conditions induced by the removal of the ears at the flowering stage. The diversion of the energies of the plant from its normal seed-bearing function proved to be without influence upon the proportion of furfural-yielding carbohydrates to total carbohydrates. The constancy of this ratio has now been established under the widest possible variations of the conditions of growth, natural and artificial, confirming the conclusions that the furfuroids are assimilated with their special constitutional characters and not formed from hexoses by subsequent processes of oxidation.

By the suppression of the seminal function of the plant, the "maturation" of the straw was virtually arrested, and this is shown by the chemical constants determined in the straw grown up to the harvesting period after removal of the ear, compared with the straw grown under normal conditions. The cellulose and "permanent tissue" are 30 and 10 per cent respectively in excess in the normal straw, and conversely the artificial product is much more readily hydrolysed by acids, and the resulting solutions (after neutralisation) are fermented by yeast to a much greater extent.

Discussion.

Dr. Voelcker, speaking from the practical and agricultural rather than from the theoretical side, enquired what was the influence of these different constituents—pentoses, hexoses, and the like—in determining the value of cereal straws at the various stages of growth. The feeding value of straw depends on the period of cutting, but the constituents determining this value were not known.

The results of the plan adopted of cutting off the ears and thus preventing formation of grain had some analogy with those obtained in keeping a clover crop closely cut down. There was an increase of root growth, and a consequent enrichment of the soil by accumulation of nitrogen. It was of interest, therefore, to know what happened in the case of cereal straws similarly treated, and in what respects enrichment took place. If the enquiry could be followed up by actual feeding experiments, some knowledge of the utility of those different complex substances at which the authors were working would be attained.

Dr. Horace Brown said that in the case of barley plants which had been deprived of their fructifying organs the increased percentage of permanent tissue and of cellulose was probably due to the accumulation in the straw of the products of assimilation which under natural conditions would have been utilised by the seed. He also expressed a hope that the authors would soon be in a position to give more definite information about the nature of the fermentable carbohydrates which are produced by the acid hydrolysis of these interesting furfuroids.

Mr. Cross, in reply, said that he hoped to give effect to some of the suggestions in a repetition of the experiments on a more extended scale during the current season.

*50. "*Isomeric Bornylamines.*" By M. O. Forster, Ph.D.

It has been observed by Leuckart and Bach (*Ber.*, 1887, xx., 104) that when camphor is heated with ammonium formate at 200°, it is converted into the formyl-derivative of bornylamine; the base from this derivative melted at 159—160°, and had the specific rotatory power $[\alpha]_D$ =

$-18\cdot6°$. By the reduction of camphoroxime with sodium and amylic alcohol, the author has obtained two bases having the empirical formula $C_{10}H_{19}N$; one of these substances melts at 163°, and has the specific rotatory power $[\alpha]_D = +45\cdot5°$, whilst the other melts at 180°, and has $[\alpha]_D = -31\cdot3°$. Having found that the base prepared by the method of Leuckart and Bach is a mixture of these two compounds, the author proposes to retain the name *bornylamine* for the dextro-rotatory base, and as the compounds are not optical antipodes, to term the isomeride *neobornylamine*.

The *formyl*, *acetyl*, and *benzoyl* derivatives, and the *hydrochloride*, *platinichloride*, *carbamide*, *phenylcarbamide*, and *picrate* of both bases have been prepared, and are described in the paper.

*51. "*Some Derivatives of Benzophenone.*" By FRANCIS EDWARD MATTHEWS, Ph.D.

Benzophenone in a moist chloroform solution very readily yields a hexachloride, $C_6H_5Cl_6{\cdot}COPh$, on saturation with chlorine and exposure to bright light.

Only one modification of this substance appears to be produced in this manner, and all attempts to introduce a further six atoms of chlorine into the molecule proved fruitless. No hexachloride could be obtained from acetophenone. Benzophenone hexachloride crystallises from xylene in brilliant colourless forms melting at 215°. It is a very stable substance, but on heating at a temperature considerably above its melting-point, evolves hydrogen chloride and benzoyl chloride, and yields a heavy yellow oil, from which trichlorobenzophenone was isolated in the crystalline state.

On decomposition with alcoholic soda, benzophenone hexachloride is decomposed in two directions. One interaction results in the elimination of hydrogen chloride and production of the trichlorobenzophenone, which crystallises from acetone on spontaneous evaporation in large hexagonal prisms or plates, and melts sharply at 131°. The second decomposition is represented by the equation $C_6H_5Cl_6{\cdot}CO{\cdot}C_6H_5 + NaOH = C_6H_6Cl_6 + C_6H_5{\cdot}CO_2Na$, and the resulting benzene hexachloride is decomposed, producing 1 : 2 : 4-trichlorobenzene. The benzoic acid produced in the hydrolysis was identified.

Benzophenonehexachloride on nitration yields a mononitro-derivative of the formula $C_6H_5Cl_6{\cdot}CO{\cdot}C_6H_4(NO_2)$, which crystallises in pale yellow needles and melts at 159°. This compound is decomposed by alcoholic soda in the same way as the parent substance. The products are 1 : 2 : 4-trichlorobenzene, metanitrobenzoic acid, a small quantity of an azo-compound, and metanitrotrichlorobenzophenone. The last substance forms pale yellow hexagonal plates from acetone and melts at 143°.

Benzophenone hexachloride dissolves in hot fuming sulphuric acid, producing a sulphonic acid. From this acid the barium salt was prepared; it crystallises in tufts of needles and contains $7\frac{1}{2}$ molecular proportions of water. It is readily decomposed by alkalis, but as the products do not crystallise well they have not been further examined.

*52. "*Experiments on Lauronolic Acid.*" By S. B. SCHRYVER, Ph.D.

An attempt was made to prepare an unsaturated isomeride from the ethylic salt of camphanic acid (oxycamphoric acid) in the same way that tetraconic acid is obtained from terebic acid (Roser, *Ann.*, 1883, ccxx., 255). Ethylic camphanate is, however, unacted upon by sodium ethoxide, the reagent used by Roser to bring about the above-mentioned reaction. Lauronolic acid was then investigated, and a method is described for its preparation on a large scale. It was oxidised with potassium permanganate, but no definite products were obtained, the acid appearing to be totally oxidised, the potassium permanganate acting on it in the same way as on the tetrahydrophthalic acids investigated by v. Baeyer. For this reason, it was thought that lauronolic acid was a hydrogenised benzene derivative. Nitric acid acts on lauronolic acid violently, yielding principally oxalic acid. In addition, however, it forms *nitrocampholactone*, a neutral product of the formula $C_9H_{13}O_2(NO_2)$, and under certain conditions this substance can be obtained in fairly large quantity. It melts at 171°, is insoluble in water, but soluble in most organic reagents. On reduction with zinc dust and glacial acetic acid, it yields the corresponding *hydroxylaminocampholactone*, $C_9H_{13}O_2(NHOH)$, which melts at 148°, reduces Fehling's solution and ammoniacal silver nitrate in the cold, and is soluble in hot water, from which it separates on cooling in the form of twinned, quadratic prisms. The hydroxylamine derivative, on oxidation with ferric chloride, yields *nitrosocampholactone*—

$$C_9H_{13}O_2(NO),$$

a bright green compound melting at 117°, and very soluble in most organic solvents. Nitrocampholactone, on reduction with tin and hydrochloric acid, yields *aminocampholactone*, $C_9H_{13}O_2(NH_2)$, a compound readily soluble in water, from which it crystallises in large, pearly plates containing water, which melt at 39°, but effloresce in a vacuum, giving an anhydrous substance melting at 66°. The platinichloride decomposes without fusion above 200°, and is a salt, not of the aminolactone itself, but of the corresponding aminohydroxy-acid—

$$[C_9H_{15}O_3(NH_2)HCl]_2PtCl_4.$$

The nitroso-compound can also be obtained by the action of nitrogen peroxide on lauronolic acid, but was not isolated, as the further action of the peroxide converts it into the nitro-compound, which, indeed, can be more conveniently prepared in this way, as the yield is greater than that obtained by the action of nitric acid. Campholactone also gives a certain amount of nitrocampholactone on treatment with nitric acid.

The hydrochloride of aminocampholactone, on treatment with potassium nitrite, yields *hydroxycampholactone*, m. p. 118°, and a liquid of sweet peppermint-like smell.

If Piloty's recent generalisation (*Ber.*, 1898, xxxi., 219), that staple nitroso-derivatives can only be derived from hydroxylamines in which the NHOH group is attached to a tertiary carbon atom, be applicable to cylic compounds, then neither the Bredt nor the Perkin formula can correctly represent the constitution of camphoric acid.

*53. "*The Drying of Ammonia and of Hydrogen Chloride.*" By H. BRERETON BAKER, M.A.

In a recent paper (*Ann.*, 1898, ccxcix., 267) Gutmann has described experiments on the action of these gases when dried. He comes to the conclusion that the drying of both gases by phosphorus pentoxide is an impossibility, because they are absorbed by the drying agent in a shorter time than is necessary to dry them. The author has repeated the experiments, and finds that this absorption of the gases, when properly purified and dried by lime and sulphuric acid respectively, only takes place when the phosphorus pentoxide is impure. When the oxide contains any quantity of metaphosphoric acid, the absorption takes place as rapidly as, and with similar results to, those described by Gutmann. From the construction of the apparatus, as well as from the similarity of the results, it is concluded that moisture was admitted while the phosphorus pentoxide was present, and that the difference between his results and those of the author published in 1894 is readily explained as due to the production of metaphosphoric acid.

With regard to the vapour density of ammonium chloride, it is pointed out that Gutmann's low results are probably due to his having collected the air, driven out of the Victor Meyer apparatus, over water and sulphuric acid instead of over boiled mercury, which was used by the author. A re-determination of the vapour density of dried ammonium chloride by Dumas's method is published in the paper. When the bulb was protected from the outer air by a phosphorus pentoxide tube terminated by a long capillary, the density of 28·8 was obtained from the dried ammonium chloride, confirming the author's con-

clusion, based on six experiments by Victor Meyer's method, that dried ammonium chloride does not dissociate at 350°.

Discussion.

Mr. Shenstone said he believed the precautions taken by Dr. Gutmann for preventing the access of water vapour to the dried ammonium chloride while determining its vapour density were insufficient, as Mr. Baker had shown; he had himself employed the very same precautions for a similar purpose in some of his earlier work on the production of ozone from oxygen, and though the results obtained were independently confirmed, and for some time accepted as correct, yet afterwards it became clear that the precautions in question had not really been sufficient for the purpose. Mr. Baker's explanation of the divergent results obtained by Dr. Gutmann and himself in their studies of the interactions of hydrochloric acid and ammonia, respectively, with phosphoric anhydride, showed the importance of using pure phosphoric anhydride for such work, and he therefore ventured to draw attention to the fact that this substance cannot be prepared by merely re-distilling the crude phosphoric anhydride. Certain precautions must be taken, *e.g.*, it is necessary to employ as low a temperature as is possible in order to avoid volatilising any metaphosphoric acid that may be present, and to seal up the product in glass tubes directly it is made.

The President said, in connection with Mr. Baker's results, it was interesting to remember that, in an elaborate paper in the *Phil. Trans.* for 1885, Professors Ramsay and Young detailed many experiments proving that the statical and dynamical vapour pressures of ammonium chloride were identical, and that the vapour pressures found at about 330° compared with the vapour density of about 15 found by them, give a calculated latent heat which amounts to about 34650 grm. units per molecule, or to about 80 per cent of the theoretical value for complete dissociation. Mr. Baker obtained a normal vapour density at 350°, or about twice that of Ramsay and Young. Assuming the tensions of the vapour to be correct, and the density to be really double that found by Ramsay and Young, then the molecular latent heat would be reduced to about one-half of the value just mentioned. But can it be assumed that the tensions of the perfectly dry salt have been determined, or that they would be identical with the values already recorded? A series of such values with ammonium chloride completely free from water, together with vapour density determinations at lower pressures, would give most valuable results, and as the real interest of the research lay in this direction, he hoped the author would attack the problem.

*54. "*Note on some of the Properties of Methylene Di-iodide.*" By H. G. Madan, M.A.

Methylene di-iodide, CH_2I_2, has for many years been used by mineralogists on account of its extremely high density (3·34 times that of water). This is, as usual, accompanied by a very high refractivity for light, which has been fully examined by Dr. Gladstone (*Trans.*, 1891, lix., 293), who found the index of refraction for yellow light (D) to be 1·756 at 10·5°, and the author has obtained nearly identical values with a different specimen. The coefficient of dispersion ($\mu_{H\gamma}-\mu_{H\alpha}=0{\cdot}062$) is decidedly higher than that of carbon disulphide, and, but for its doubtful permanency in light, methylene di-iodide might advantageously replace the latter substance in spectroscope prisms, especially as its boiling-point is very high (181°), and as it is practically non-inflammable. A few hours' exposure to strong sunlight turns it a light orange colour, and an exposure of ten days deepens this to a red tint.

At a temperature of 100° sulphur dissolves in methylene di-iodide fairly easily, but some crystallises out on cooling; enough, however, remains in solution at ordinary temperatures to raise the index for D to 1·778.

Methylene di-iodide dissolves phosphorus readily and abundantly; in fact, its own weight (or, taking into account the relative densities, about twice its volume) of phosphorus may be dissolved in it without reaching the point of saturation at ordinary temperatures. The resulting light yellow liquid has, as might be predicted, a very high refractivity, the index of refraction for the D line being 1·95 at 14°. The third decimal place is not given, owing to a fact not readily explained, which was also noticed by Gladstone and Dale (*Phil. Mag.*, 1859, [iv.], xviii., 30), in dealing with solutions of phosphorus in carbon disulphide; viz., a difficulty in obtaining a sharp image of the spectrometer slit through the solution. The solution is, unfortunately, readily acted on by light, like similar solutions of phosphorus, a deposit of red phosphorus being formed.

This solution is far safer to deal with than the solution of phosphorus in carbon disulphide. A few drops poured on filter-paper may be left freely exposed to the air for hours, and even days, without catching fire, the scarcely inflammable solvent seeming to form a kind of varnish over the phosphorus which protects the latter from rapid oxidation.

Discussion.

Mr. Vernon Harcourt suggested that the presence of phosphorus in the methylene di-iodide might serve the incidental purpose of preventing the colouration of the liquid when exposed to light.

The President asked if Mr. Madan had observed that the production of free iodine on exposure to light was in any way dependent on the presence of oxygen or traces of water. In the case of carbon disulphide, to which the author had referred as giving a deposit in prisms on exposure to light, this was certainly caused by a secondary action, which involved the presence of water, since perfectly dry carbon disulphide enclosed in sealed tubes, and exposed to sunlight, in presence of a dehydrating agent like sulphuric acid did not form any deposit.

Mr. Madan, in reply to Mr. Harcourt, said that he was afraid that the phosphorus did not seem to have the hoped-for result. In fact, the traces of iodine liberated appeared (as was noticed long ago by Sir B. C. Brodie, *Trans.*, 1853, v., 289) to hasten the conversion of the phosphorus into the red allotropic form; and the solution, whether in a sealed tube or in an open watch-glass, eventually solidified to an orange or red mass. In reply to the President, he said that the methylene di-iodide had been dried as far as possible by calcium chloride before being placed in the tubes for exposure to light, but he would take an early opportunity of ascertaining the result of a more careful and complete desiccation.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, April 22nd, 1898.

Mr. Shelford Bidwell, President, in the Chair.

A paper by Prof. T. C. Porter, on "*A Method of Viewing Newton's Rings*," was read by Prof. S. P. Thompson.

If a parallel beam of light from a rectangular slit falls at oblique incidence upon a plane plate of glass, the first two reflections occur at the upper and lower surfaces of the glass respectively, and give two corresponding images that may be formed on a screen. If now, a second glass plate is added below the first, and parallel to it, at a short distance, four images of the slit appear on the screen. But when the lower plate is brought into contact with the upper one, the reflection from the lower surface of the upper plate follows the same path as that from the upper surface of the lower plate, so that only three images are now to be distinguished. For the two glass plates the author substitutes a "Newton's rings" apparatus, and by the above device for eliminating a set of reflections

he is able to restrict the illumination to the light that comes from the two interior surfaces. As thus observed, the colours of the rings are very brilliant. When the plates are very clean, the darkest area of the "black" spot has a sharply-defined edge, similar to that of the black film of a soap-bubble. By using monochromatic light the various sets of rings may be photographed; they appear as several systems of concentric circles, the systems intersecting one another. This method of illumination by a slit enables Newton's rings to be viewed free from all light except that due to reflections at the bounding surfaces of the air-space between the plates. It reveals to the eye the subordinate interference-systems that coexist with the primary rings, and it demonstrates which of these reflections must be taken into account in the theory of the phenomenon. Moreover, it supplies a means for analysing these systems, and it indicates that the interference of monochromatic light is never complete under these circumstances.

Prof. Herschel said it was rather difficult to follow the arguments of the author without witnessing the phenomena. Much complication was introduced by the successive reflections; it was not clear what became of them. There was no doubt as to the advantage of a narrow slit for the illumination. He thought some of the secondary reflections might be got rid of by using plates that were slightly prismatic.

Prof. Thompson had, in his own laboratory, verified the advantages of the author's method of illumination. The result was a very sharply-defined first system of rings. Curves of subordinate interference were easily to be observed by this arrangement.

Prof. Boys noticed in the photograph of the ring-systems that the independent systems of bands were distorted at the points of intersection. The intersecting curves formed a sort of honeycomb, or hexagonal system, instead of a system of curvilinear quadrilaterals. This distortion reminded him of similar effects observed in the photographs of "ripples."

Mr. Edser said he had often noticed similar distortions, but he had always been able satisfactorily to explain them as being the result of imperfect focussing. The author had referred to the fact that a thin film when viewed by reflected light appears black. A phase-change of half a wave-length takes place either on reflection at a rarer or at a denser medium; but there is no information from which to decide between these two alternatives. The truth of the assumption that the phase-change occurs at the denser medium seems to depend, so far as experimental evidence is concerned, upon the observation that in Lloyd's bands the central one is black. To produce the Lloyd's bands only one mirror is used; the bands produced by Fresnel required three mirrors. Wernicke performed an interesting series of experiments, in which white-light reflected for various angles of incidence from a thin sheet of glass was examined spectroscopically. The spectrum was crossed by numerous black bands, and from the position of these bands in the spectrum the thickness of the glass was calculated. The calculated thickness when the angle of incidence was great differed from that obtained with small angles of incidence; the conclusion was that when light is internally reflected, even at an angle of incidence less than the angle of total reflection, a phase-change is produced. If the space between the two plates in Prof. Porter's experiment were filled with a substance of higher refractive index than glass, a confirmation, or otherwise, of this result might be obtained.

Dr. S. P. Thompson then exhibited a model apparatus, made by the Helios Company, to illustrate the three-phase method of transmitting power. It consists of a small generator, driven by hand, and a small motor. The generator may be separately excited by a secondary battery; it has three independent coils. The six ends of the coils are connected to six commutator rings. The motor has three corresponding pairs of opposite coils; these can be grouped in various ways for connection to the brushes of the generator. The six coils are on a hinged frame, so that if necessary they can be laid down flat for other rotation experiments. Two armatures are provided, either of which may be used. The first is an iron wheel with peripheral copper bars, arranged like a squirrel-cage; the other is a simple iron disc, without added conductors.

The President proposed votes of thanks, and the meeting was adjourned until May 13th.

NOTICES OF BOOKS.

The Tutorial Chemistry. Part II. Metals. By G. H. Bailey, D.Sc. Lond., Ph.D. Heidelberg. Edited by William Briggs, M.A., F.C.S., F.R.A.S. London: W. B. Clive, University Correspondence College Press. 1897. Pp. 300.

It is assumed that the student has spent at least one year at chemistry before taking up the volume now before us. It is, in fact, more a metallurgical than a chemical work pure and simple, as the manufacturing methods of producing the metals appear to be among its principal features. The first few chapters have to do with atomic weights and the relations between them; the constitution of gaseous and liquid compounds; solution; as well as the nature of chemical reaction, where it is shown that chemical changes are in reality much more complex than they at first sight appear to be. In many cases a careful examination will show that, alongside the main reaction indicated in the equation, secondary reactions are also going on. In chap. viii. we begin with the alkalies, K, Rb, Cs, (Am), Na, Li, their preparation and compounds, followed in the next chapter by the alkaline earths, Ca, Sr, Ba; but we must admit being a little surprised to find in chap. xii. that copper is included with gold, silver, and platinum as a noble metal. Its method of production and manufacture differs *in toto* from those of the other three. The only apparent reason for this seems to be that gold and silver are sometimes found associated with copper. Then in succeeding chapters follow the iron, manganese, chromium, tin, and arsenic groups, all of which are well treated considering the small amount of space available for each. There are three appendices—(1) on crystallisation and crystallography; (2) spectrum analysis; and (3) a list of experiments suitable to each chapter. A good index of eleven pages closes the book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 12, March 21, 1898.

Reaction of some Reagents on Carbonic Oxide, with Regard to the Analysis of the Air of Towns.—Armand Gautier.—When carbonic oxide is present in the air to the extent of some hundredths, as in the case of the gaseous products of fires and factories, its estimation is simple, by means of absorbing it in acid cuprous chloride. But when it is present only in thousandths or ten-thousandths instead of hundredths, this method—even with M. Saint-Martin's excellent modifications—is of no value. Ammoniacal nitrate of silver cannot be depended on if other reducing agents are present. Permanganate of potash at 1/10000th is reduced very slowly in the cold by carbonic oxide, though at 1/100th its action is more rapid. Iodic acid at 1/100th will not oxidise carbonic

oxide in the cold, but at 1/10th and 100° the action is very marked. Chloride of gold at 1/100th is an excellent reagent; with the pure gas the action is almost immediate.

On Neodymium.—O. Boudouard.—(See p. 193).

Some Properties of Phosphorescent Sulphide of Strontium.—J. R. Mourelo.—The author has made mixtures of a sulphide of strontium, having a very strong phosphorescence, with inert bodies, such as sulphate of strontium, barium, or calcium. The results showed that, although the mass became phosphorescent in a uniform manner, the intensity of the light is less when the added sulphate has a low specific gravity than when it has a higher one.

Oxidation of some Amide and Thioamide Compounds.—Œchsner de Coninck.—The author describes his experiments on the action of the alkaline hypochlorites in the presence of an excess of alkali, on acetamide, sulpho-urea, phenyl-urea, phenyl-sulpho-urea, methyl-glycocol, and oxymethane.

Chloridised Derivatives of Carbonate of Phenyl.—E. Barral.—The bi-chloridised carbonate of phenyl, $CO(OC_6H_4Cl)_2$, has been obtained; it crystallises in white silky needles which melt at 142°, are insoluble in water, only slightly soluble in the cold in benzene and absolute alcohol, though easily so when boiled.

Zeitschrift für Anorganische Chemie,
Vol. xvi., No. 4.

Oxycobaltamines and Anhydroxycobaltamines.—Alb. Mylius.—(1) The author prepares anhydroxycobalt nitrate by acting upon a solution of cobalt carbonate in dilute nitric acid with ammonium nitrate. The raw product is purified by dissolving in hot water containing nitric acid, and, on cooling, the nitrate separates in black needles, which on analysis are found to have the composition $Co_2O_2(NH_3)_{10}(NO_3)_5$. Anhydroxycobalt chloride is prepared from the nitrate by treating the latter three times with cold concentrated HCl and allowing it to stand for an hour. The green chloride, crystallised from hot water (containing HCl), is obtained in long green needles of composition $Co_2O_2(NH_3)_{10}Cl_5+H_2O$. Ammonia acts on the nitrate when solutions of the two are shaken up and then concentrated by evaporation. A yellow nitrate separates which has the composition $Co(NH_3)_6(NO_3)_3$. Potassium cyanide acts on the nitrate, with evolution of HCN and NH_3, forming a cyanide. (2) To prepare chloropentaminecobalt chloride, the freshly-prepared oxycobaltamine nitrate is dissolved in sulphurous acid, and the whole decomposed by strong HCl, when small quantities of the salt are formed. Various oxycobaltamine salts are also prepared.

Quantitative Estimation of Manganese, and the Separation of Iron and Manganese by Electrolysis.—Friedrich Kaeppel.—Manganese can be estimated electrolytically by using a neutral or slightly acid solution, when the manganese is deposited partly as the metal, partly as peroxide. The current must, however, be very strong, and the results are not very satisfactory. The author finds that, by addition of acetone to the solution, much better results are obtained; the precipitate of MnO_2 being obtained as a fine powder. A table of experimental results is given, which agree very well with the calculated ones. The author also attempts the quantitative separation of iron and manganese electrolytically by adding H_3PO_4 to the solution of the sulphates, which succeeds fairly well.

Pervanadic Acid.—Anton Scheuer.—The author prepares barium pervanadate by decomposing a saturated solution of ammonium meta-vanadate in water containing peroxide of hydrogen, by means of barium chloride solution. The barium pervanadate falls as a heavy amorphous yellow precipitate, which must be washed with water containing peroxide until all the ammonium chloride is removed, and then dried over calcium chloride. The reaction may be represented by the equations—

$$\begin{cases}(NH_4)VO_3+H_2O_2=(NH_4)VO_4+H_2O\\2(NH_4)VO_4+BaCl_2=Ba(VO_4)_2+2NH_4Cl.\end{cases}$$

The $Ba(VO_4)_2$ can be analysed by measuring the oxygen split off on the addition of dilute sulphuric acid and slightly warming. The reaction is finished when the red colour of the solution has changed to bright green. The vanadic acid present is titrated against standard permanganate solution. Various other pervanadates are also prepared and analysed.

MEETINGS FOR THE WEEK.

Monday, May 2nd.—Royal Institution, 5. (Annual Meeting).
—— Society of Arts, 8. (Cantor Lectures). "The Electric Locomotive," by Prof. Carus Wilson.
—— Society of Chemical Industry, 8. "Self-intensive Refrigeration of Gases, Liquid Air, and Oxygen," by Dr. W. Hampson.
Tuesday, 3rd.—Society of Arts, 8. "Senefelder and the Centenary of Lithography, 1798-1898," by Joseph Pennell.
—— Royal Institution, 3. "The Historical Development of Europe," by Samuel Rawson Gardiner, M.A., D.C.L., LL.D.
Wednesday, 4th.—Society of Arts, 8. "The Revival of Hand-loom Weaving," by Miss Clive-Bayley.
Thursday, 5th.—Chemical, 8. "The Reaction of the Carbohydrates with Hydrogen Peroxide," by C. F. Cross, E. J. Bevan, and Claud Smith. "The Properties and Relationships of Dihydroxytartaric Acid," Part II., by H. J. H. Fenton, M.A. "The Affinity Constants of certain Hydroxy-acids," by S. Skinner, M.A. "Molecular Weights in Solutions of Permanganates, Perchlorates, and Periodates," by J. Murray Crofts, B.A., B.Sc.
—— Royal Institution, 3. "Some Leaders in the Poetic Revival of 1760-1820—Cowper, Burns, and Scott," by The Rev. Canon Ainger, M.A., LL.D.
Friday, 6th.—Royal Institution, 9. "Living Crystals," by Edward A. Minchin, M.A.
Saturday, 7th.—Royal Institution, 3. "Programme Music" (with Musical Illustrations), by Sir Walter Parratt, Mus. Doc., Master of the Queen's Music.

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THE CHEMICAL NEWS.

VOL. LXXVII., No. 2006.

APPARATUS FOR DETERMINING THE COMPOSITION OF AMMONIA, SULPHUR DIOXIDE, WATER, &c.

By GEORGE GEORGE, A.I.C., F.C.S.

THE apparatus shown in the sketch can be used for determining the composition (completely or in part) of a number of gases, and has been found exceedingly useful for lecture-room experiments.

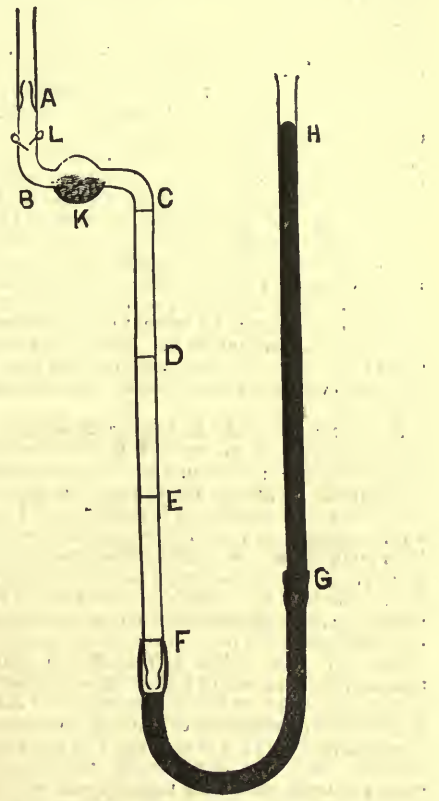
It consists of a bent glass tube, A F, connected by means of a piece of thick-walled rubber tubing to the glass pressure tube, G H. The tube A F is made of Jena glass of about ¼ inch bore. The lengths of the limbs of the tube are as follows:—A B and B C each about 3 inches, and C F about 24 inches. A pair of platinum wire electrodes are fused into the tube at L, and a small bulb is blown at K. Before use, the tube is graduated into four parts; the volumes between A and C, C and D, D and E, and E and F being equal. Marks are made at the points C, D, E, and F by means of a file or, preferably, by the use of hydrofluoric acid.

Determination of the Composition of Ammonia Gas.—The tube A F, having been graduated and thoroughly cleaned and dried, is attached by means of the rubber tubing to the pressure tube H G. A short piece of rubber is also attached at A; in all cases the rubber should be wired on to the glass tubes. Clean *dry* mercury is poured into the pressure tube, and the latter is then raised until the whole of the tube A F is filled with mercury. When this is the case, a screw-clip is placed over the rubber tube at A: A F is now ready for filling with *dry* ammonia. Ammonium hydrate is gently heated and the gas passed through two lime towers to dry it. When it is issuing freely, the delivery-tube is connected with A F by means of the rubber tube at A, and the clip opened. On lowering the pressure-tube, A F is soon filled with the gas, and the clip is then replaced. A short thistle-headed funnel is attached at A, and in it is placed some *fine freshly-ignited* cupric oxide. The pressure tube is raised so that the gas in A F is under pressure, and the clip then opened. The cupric oxide enters the tube, and at the same time some of the ammonia escapes. This prevents any air from entering the tube when the copper oxide is being admitted. Ammonia is allowed to escape until A D is just filled with the gas at atmospheric pressure. By gently tapping the tube, the copper oxide can be made to occupy the bulb K, as shown in the sketch.

The electrodes at L are now connected with a powerful induction coil, and sparks passed. After some time the volume of the gas will almost have been doubled; and when allowed to cool, and the pressure adjusted, the gas will occupy A F (nearly). The bulb K is now heated, first gently and finally to redness. The copper oxide is reduced by the hydrogen, and when all action is over and the apparatus has been allowed to cool down, the residual gas (nitrogen) will be found to occupy A C; that is, two volumes of ammonia gas are composed of three volumes of hydrogen and 1 volume of nitrogen.

To show that *sulphur dioxide* contains its own volume of oxygen, the tube A F is filled with dry oxygen, and pure sulphur is then admitted. The oxygen is allowed to escape until A D only is occupied by the gas. The portions of tube A B and C D are then heated by means of the Bunsen, and finally the bulb K, which contains the sulphur. When the sulphur takes fire, the flames spread in both directions, and all the oxygen is converted into sulphur dioxide. On allowing the tube to cool and adjusting the pressure, the original volume is found to be unchanged. Therefore sulphur dioxide contains its own volume of oxygen. On allowing a strong solution of potassium bichromate to enter at A, all the gas is absorbed.

To prove that *water* contains two volumes of hydrogen and one volume of oxygen, fill A D with oxygen and then pass in hydrogen until A F is full; that is, there will be two volumes of hydrogen and two volumes of oxygen in the tube. Clamp firmly and spark. On adjusting the pressure, A C will be full of oxygen.



The experiment can then be repeated using one volume of oxygen and three volumes of hydrogen.

The apparatus can also be used for showing that nitrous oxide contains its own volume of nitrogen, whilst nitric oxide contains half its volume of nitrogen. In each case potassium is used to decompose the gas. By using dry air and phosphorus, it can be shown that air consists of a mixture of four volumes of nitrogen to every one volume of oxygen.

This apparatus can be supplied by Messrs. Baird and Tatlock, of London and Glasgow.

Allan Glen's School
(Glasgow and West of Scotland Technical College).

The Behaviour of some Salts of Platinichlorhydric Acid.—Paul Rohland.—This paper is a continuation of one on the dissociation phenomena of some salts of platinichlorhydric acid with regard to solutions in alcohol and water. It is found that certain salts, as $MgPtCl_6$ and $MnPtCl_6$, crystallise with different numbers of molecules of water at different temperatures, while at temperatures below −3° they separate into their components.—*Zeit. f. Anorganische Chemie*, xvi., No. 4.

ON AN IODIDE OF TUNGSTEN.

By E. DEFACQZ.

Various reactions have been tried for the preparation of iodide of tungsten. Von Borch tried, without success, the action of the vaporised chloride on iodide of potassium and on iodide of silver, and he had no more success in passing a mixture of the vapour of the same chlorides and hydriodic acid in a tube heated to redness. M. Riche was the first to announce the existence of an iodide of tungsten; Professor (now Sir Henry) Roscoe, in his well-known paper on the halogen compounds of this metal, gave its composition. These two great authorities obtained it by the action of iodine on the metal itself, prepared by the reduction of tungstic acid by hydrogen.

The action of dry hydriodic acid having in several cases given very good results we thought it would be as well to utilise this reaction.

Method of Preparation.—The melted metal, prepared by the use of the electric furnace according to the method adopted by Moissan (*Comptes Rendus*, cxxiii., 13), is placed in a boat in the middle of a green glass tube, through which a current of chlorine is kept flowing; it is heated up to a dull red heat, using the precautions recommended by Sir Henry Roscoe. The pure sublimated hexachloride is thus obtained. The chlorine gas is then driven out of the apparatus by means of a current of dry carbonic acid gas, after which a current of dry gaseous hydriodic acid is passed for an hour, while heating that part of the tube nearest to where the hexachloride was first placed to about 400°.

At the commencement of the reaction there is an abundant deposition of iodine, and finally a brown infusible mass is obtained; this must be first washed with pure and dry sulphide of carbon, to get rid of the small quantity of free iodine still present; it is then air-dried and taken up with alcohol at 95°, and finally dried in the oven at 116°. This method requires several precautions: the temperature must not go above 500°, so as to avoid the commencement of the reduction by the hydriodic acid which would otherwise occur, it being preferable to operate on the sublimated hexachloride rather than on the same substance melted.

Analysis.—The iodide is placed in a boat in a glass tube and then heated in a slow current of air; the iodine which is given off by the decomposition is drawn off into a convenient receptacle containing an aqueous solution of sulphurous acid; it is estimated in the form of iodide of silver, and then transformed into the chloride as a matter of verification; the tungstic acid which remains in the boat is weighed; from its weight the quantity of the metal present is deduced.

By this method we found—

	Found.			Calculated for WI_2.
W	42·16	42·20	42·24	42·01
I	—	56·82	57·40	57·99
		99·02	99·64	100·00

Properties.—Iodide of tungsten, WI_2, exists in the form of a brown amorphous powder, insoluble in water, sulphide of carbon, or alcohol.

It is infusible, cannot be volatilised without decomposition, giving on contact with the air iodine and tungstic acid. Its density at 18° is 6·9.

Hydrogen is without action until about 500°; above this temperature the iodide is reduced, with loss of iodine.

Chlorine attacks it at about 250°, and gives the corresponding chloride; if the temperature be further increased, compounds containing more chlorine are formed.

Bromine only gives the corresponding bromide at about 350°.

Sulphur and phosphorus give corresponding compounds.

Water only acts very slowly in the cold, but more rapidly on boiling; by steaming, the blue oxide is formed.

Carbonic acid has no action until about 500°, and it then gives a brown body, non-volatile and infusible, and which, under the influence of a slight elevation of temperature, burns in the air like tinder, forming tungstic acid.

Gaseous hydriodic acid acts in the same way as does hydrogen at about 500° to 600°.

The aqueous solutions of hydrochloric and hydrofluoric acids only attack it very slowly. Nitric and sulphuric acids and aqua regia decompose it on boiling, and leave a residue of tungstic acid.

Iodide of tungsten is easily attacked by an aqueous solution of potash, and with great vigour, giving off iodine, by melted potash, also by melted alkaline carbonates and mixtures of the nitrates and carbonates.

To sum up, it is very easy to prepare the iodide WI_2 by the action of dry hydriodic acid on pure hexachloride of tungsten.—*Comptes Rendus*, vol. cxxvi., No. 13.

ON THE YTTRIC EARTHS CONTAINED IN THE MONAZITE SANDS.*

By P. SCHÜTZENBERGER and O. BOUDOUARD.

(Concluded from p. 195).

In the whole of the preceding work the process consists essentially of separating as near as possible equal quantities of sulphates, starting from a solution of yttric sulphates, and of analysing the different portions. As the results show, starting with an average atomic weight of 105, we gradually arrive at a series of figures varying from 93·9 to 111·3. In the hope of obtaining better and more rapid results, we changed the method of working. Starting with a solution of yttric sulphates, we crystallised almost the entire quantity, leaving only enough mother-liquor to give on evaporation to dryness 1 or 2 grms. of anhydrous sulphate. The first crystals obtained, after dehydration, were dissolved in cold water, and the solution treated as we have just described. This method has been applied to sulphates which gave on analysis, as atomic weights of the corresponding metals, figures varying from 104·9 to 106·2. Ten operations similar to the one described above were made.

First Residual Mother-liquors.

Atomic weight .. .. 98·9
Anhydrous sulphate used .. 1·1065
Oxide obtained .. .. 0·5600

Second Residual Mother-liquors.

Atomic weight .. .. 99·3
Anhydrous sulphate used .. 2·0725
Oxide obtained .. .. 1·0520

Third Residual Mother-liquors.

Atomic weight .. .. 101·5
Anhydrous sulphate used .. 1·0925
Oxide obtained .. .. 0·5585

Fourth Residual Mother-liquors.

Atomic weight .. .. 102·8
Anhydrous sulphate used .. 1·2387
Oxide obtained .. .. 0·6365

Fifth Residual Mother-liquors.

Atomic weight .. .. 103·3
Anhydrous sulphate used .. 1·2210
Oxide obtained .. .. 0·6285

Sixth Residual Mother-liquors.

Atomic weight .. .. 101·5
Anhydrous sulphate used .. 0·6210
Oxide obtained .. .. 0·3175

* *Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 6.

Seventh Residual Mother-liquors.

Atomic weight .. .. 104·35
Anhydrous sulphate used .. 1·6935
Oxide obtained .. .. 0·8763

Eighth Residual Mother-liquors.

Atomic weight .. .. 104·5
Anhydrous sulphate used .. 2·0670
Oxide obtained .. .. 1·0700

Ninth Residual Mother-liquors.

Atomic weight .. .. 106·0
Anhydrous sulphate used .. 1·6529
Oxide obtained .. .. 0·8603

Tenth Residual Mother-liquors.

Atomic weight .. .. 109·1
Anhydrous sulphate used .. 1·7215
Oxide obtained .. .. 0·9055

Finally the analysis of the crystals corresponding to these last mother-liquors gave the following result:—

Atomic weight .. .. 114·4
Anhydrous sulphate used .. 1·9173
Oxide obtained .. .. 1·0270

B α.—The oxides which gave atomic weights varying from 102·8 to 104·5 were mixed and converted into sulphates. Three successive crystallisations were made:—

B α (1).

Atomic weight .. .. 104·2
Anhydrous sulphate used .. 3·2715
Oxide obtained .. .. 1·6900

B α (2).

Atomic weight .. .. 100·95
Anhydrous sulphate used .. 2·3667
Oxide obtained .. .. 1·2072

B α (3).

Atomic weight .. .. 95·7
Anhydrous sulphate used .. 0·9084
Oxide obtained .. .. 0·4537

A α.—The oxides which gave atomic weights varying from 99·7 to 102·8 were treated in the same manner as B α. The sulphates were crystallised and five portions separated, which gave on analysis the following results:—

A α (1).

Atomic weight .. .. 102·15
Anhydrous sulphate used .. 2·3209
Oxide obtained .. .. 1·1902

A α (2).

Atomic weight .. .. 102·7
Anhydrous sulphate used .. 2·4845
Oxide obtained .. .. 1·2773

A α (3).

Atomic weight .. .. 101·9
Anhydrous sulphate used .. 2·4267
Oxide obtained .. .. 1·2424

A α (4).

Atomic weight .. .. 100·3
Anhydrous sulphate used .. 2·3595
Oxide obtained .. .. 1·2005

A α (5).

Atomic weight .. .. 96·5
Anhydrous sulphate used .. 0·5456
Oxide obtained .. .. 0·2736

According to these results we were able to predict the existence of an earth of which the atomic weight of the metal would be equal to 102; the three first deposits representing nearly the whole of the sulphates used. Admitting this hypothesis, the formula of the hydrated sulphates obtained from all these fractionations would be $(SO_4)_3N_2,8H_2O$. This formula corresponds to 22·6 per cent of water of crystallisation; experiment has always given figures varying around 22 per cent.

In any case, if we had here to deal with a definite body, we ought, after further fractional crystallisations, to get no sensible variations in the value of the atomic weight found. For this purpose A α (1), A α (2), and A α (3) were mixed and submitted to a new series of crystallisations. The mixture was registered as A α No. 2. The results were as follows:—

A α No. 2 (1).

Atomic weight .. .. 103·4
Anhydrous sulphate used .. 3·0900
Oxide obtained .. .. 1·5912

A α No. 2 (2).

Atomic weight .. .. 101·7
Anhydrous sulphate used .. 2·5080
Oxide obtained .. .. 1·2830

A α No. 2 (3).

Atomic weight .. .. 98·7
Anhydrous sulphate used .. 0·5350
Oxide obtained .. .. 0·2705

The two first crystallisations of A α No. 2 (103·4 and 101·7) were mixed. The oxide obtained by calcining the sulphates at a very bright red heat was dissolved in nitric acid and transformed into sulphate; this sulphate was crystallised, and three portions were obtained, but only the two last were analysed, with the following results:—

A α No. 3 (2).

Atomic weight .. .. 100·4
Anhydrous sulphate used .. 0·6158
Oxide obtained .. .. 0·3135

A α No. 3 (3).

Atomic weight .. .. 96·5
Anhydrous sulphate used .. 0·4170
Oxide obtained .. .. 0·2090

The sulphate A α No. 3 (1) was calcined and the oxide converted into sulphate, crystallised, and the mother-liquors only, marked as A α No. 4 (2), were analysed.

A α No. 4 (2).

Atomic weight .. .. 98·9
Anhydrous sulphate used .. 0·6726
Oxide obtained .. .. 0·3403

A α No. 4 (1) was treated in the same manner as A α No. 3 (1), with the following results:—

A α No. 5 (1).

Atomic weight .. .. 103·5
Anhydrous sulphate used .. 1·8865
Oxide obtained .. .. 0·9720

A α No. 5 (2).

Atomic weight .. .. 99·6
Anhydrous sulphate used .. 1·0248
Oxide obtained .. .. 0·5198

A α No. 5 (1) was treated in the same manner as A α No. 3 (1) and A α No. 4 (1), and the mother-liquors only were analysed:—

A α No. 6 (2).

Atomic weight .. .. 97·5
Anhydrous sulphate used .. 0·7535
Oxide obtained .. .. 0·3791

A α No. 6 (1) was treated in the same manner as A α No. 3 (1), A α No. 4 (1), and A α No. 5 (1), and three

crystallisations were made, which on analysis gave the following results :—

A α No. 7 (1).

Atomic weight	104·8
Anhydrous sulphate used ..	2·3485
Oxide obtained	1·2158

A α No. 7 (2).

Atomic weight	98 1
Anhydrous sulphate used ..	0·4479
Oxide obtained	0·2259

A α No. 7 (3).

Atomic weight	96·05
Anhydrous sulphate used ..	0·4319
Oxide obtained	0·2160

A α No. 7 (1), after undergoing a treatment analogous to what has just been described, gave these results :—

A α No. 8 (1).

Atomic weight	104·87
Anhydrous sulphate used ..	3·9965
Oxide obtained	2·0695

A α No. 8 (2).

Atomic weight	99·9
Anhydrous sulphate used ..	1·2705
Oxide obtained	0 6455

Finally, A α No. 8 (1), after a repetition of the same treatment, gave the two following crystallisations :—

A α No. 9 (1).

Atomic weight	104·65
Anhydrous sulphate used ..	3·1230
Oxide obtained	1·6160

A α No. 9 (2).

Atomic weight	101·5
Anhydrous sulphate used ..	1·0405
Oxide obtained	0·5320

In this last series, before commencing a fractional crystallisation, the sulphate was always calcined. One might imagine that a calcination at a white heat would facilitate the separation of the earths ; as a matter of fact, the sulphates obtained after the solution of the oxide in sulphuric acid showed differences in solubility much more marked, and thus allowed of a much sharper and more rapid fractionation.

According to these several series of results, it is evident that the method of fractional crystallisation is not to be very much depended on for separations ; a time arrives when we keep getting a practically constant number during several crystallisations, but at length this figure disappears, to make room for another one. In the hope of getting rid of this cause of uncertainty, we have adopted a method of *fractional fusions*, the results of which will form the subject of our next paper.

THE LINE SPECTRUM OF SILICON.

By J. M. EDER and E. VALENTA.

In a former paper, we have given an account of our investigations on the wave-lengths of the emission spectrum of silicon.

To study this spectrum, we used a spectrograph with one quartz prism, and therefore obtained a spectrum which naturally showed in the less refracted parts a proportionately small dispersion. Since then, we have used a large grating spectrograph, and revised all the results obtained by the former method. We used as standard lines a number of those measured by Rowland, the iron lines measured by Kayser, and the copper lines we had formerly measured ourselves. By the use of these we were able to estimate the wave-length of the silicon lines with the greatest accuracy.

First we satisfied ourselves as to the coincidence of the chief silicon lines in the arc spectrum, as measured by Rowland, with the lines in the spark spectrum. We could not find Rowland's line λ=2263·507 in the spark spectrum of silicon, but we confirmed the existence of a line which had already been measured, λ=2542 (accurately, λ=2541·89), as well as a number of diffused violet and some weak ultra-violet lines. Some very feeble lines of the silicon spectrum could only be obtained with the quartz apparatus and not with the grating—probably on account of the greater amount of light obtainable by the former apparatus.

For investigating the silicon spectrum, we took two alloys—one of silicon and copper and the other of silicon and magnesium. These alloys were used as electrodes—or, equally well, could be used carbon or zinc electrodes—between which, during the passing of an alternating spark, silicon chloride was allowed to drop. By using electrodes of the element silicon, the same results were obtained.

We emphasize once again that the characteristic group of lines, which are defined very sharply, lie in the ultra-violet, so that the identification of silicon spectroscopically is very easy with a quartz spectrograph, but scarcely possible with glass prisms.

The following table contains the results of our measurements related to Rowland's normal line. They extend from λ=4131 into the ultra-violet part of the spectrum :—

Wave-length.	Intensity.	
4131·0	4	Diffused.
4128·2	4	
3905·80	3	
3862 75	3	Diffused.
3856 20	3	
3854·00	1	Diffused ; indistinct.
3834·4	1	
3826·7	1	
3795·9	2	
3791·1	1	
3191·1	1	
3086·8	1	
2987·77	4	
2881·70	10	Sharp line.
2689·8	1	
2677·4	1	
2673·3	1	
2659·0	1	
2631·39	8	Sharp line.
2568·8	2	
2541·89	8	Sharp line.
2534·7	1	
2533·2	4	
2528·60	8	Especially characteristic group of lines.
2524·21	8	
2519·30	8	
2516·21	10	
2514·42	7	
2506·99	8	
2479·8	1	
2452·22	3	
2446·0	3	
2443·46	2	
2438·86	2	
2435·25	8	Sharp line.
2356·9	1	
2303·3	1	
2219·5	1	
2218·15	1	
2216·76	4	Characteristic group of lines.
2211·8	3	
2210·9	3	
2208·1	3	
2122·8	2	Sharp line.
1929·0	1	

ON THE CORROSION OF ALUMINIUM.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, New South Wales.

In order to ascertain the effects of the weather upon ordinary sheet aluminium, two shallow dishes were made of 1 m.m. or $\frac{1}{25}$-inch gauge metal, and exposed on the roof of the chemical laboratory of this University from November 23rd, 1893, to December 7th, 1894, or fifty-four weeks.

The metal was made into basins, so as to catch rain-water, and to give the salts, &c., which it might have in solution, a longer time to act upon the metal.

The metal very soon lost its brilliancy, and became somewhat rough and speckled with grey spots mixed with larger light-grey patches; it also became rough to the touch. The grey parts could be seen to distinctly project above the surface, and under the microscope they presented a blistered appearance. This incrustation is held tenaciously and does not wash off, neither is it removed on rubbing with a cloth.

The raised parts are probably due to the formation of a hydrated oxide, but I am leaving the determination of the composition of this until I have a larger quantity at my disposal.

Contrary to my expectations, the cups had not lost weight, but had even increased.

One weighing 13·91 grms. had increased by 0·104 grm., and the other, weighing 13·865 grms., increased by 0·080 grm. After boiling in water for some hours and rubbing, the first still showed an increase of 0·077 grm., and the second of 0·055 grm.

To ascertain the effects of common salt, a plate of the same metal, 3×4 inches, and weighing 19·829 grms., was repeatedly dipped in a solution of sodium chloride, and allowed to dry; the alternate dipping and drying was repeated almost daily for three months; the plate lost 0·019 grm., and after washing and rubbing dry 0·059 grm.

My reason for making these experiments is that Mr. H. C. Russell, C.M.G., F.R.S., the Government Astronomer, some years ago tried aluminium cups for a rain-gauge, but found that they were so quickly corroded through that he had to relinquish the use of the metal. If they had been gilt they might, however, have answered well enough. Then, too, it is a very common thing to see aluminium recommended for certain architectural work on account of its lightness and its assumed permanent lustre, this assumption being due to the statements, repeated from book to book, that aluminium is unaltered by exposure to the air, that it is unacted upon by water, hydrogen sulphide, and only slightly by dilute acids—even in modern special treatises such as "Aluminium," by Joseph W. Richards, M.A., London, 1890.

The absolutely pure metal may be permanent in the air, but the best aluminium ordinarily obtainable is in that respect very little, if at all, superior so zinc.

Recently it has been found that sea-water acts upon aluminium with some quickness; hence it is not so perfect a material for torpedo and other boats as was previously thought.

Hence the prevalent idea that aluminium is a metal resembling gold or silver in the property of not oxidising must be relinquished.—*Proceedings of the Australasian Association for the Advancement of Science*, 1895.

Messrs. Perken, Son, and Rayment announce that they have recently perfected a small camera for use in the hand or on a tripod stand; they call it the "Optimus" Ubique improved hand camera. It is suitable for snap-shots, landscapes, and portraits, and is fitted with a rising front and also with a horizontal and vertical swing-back. It is a convenient little instrument, and should go well in the coming "shooting" season, especially as the price is not high.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 21st, 1898.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 199).

55. "*The Condensation of Chloral Hydrate with Orcinol.*" By J. T. Hewitt, M.A., D.Sc., and F. Dixon, B.Sc.

The authors have re-investigated the substance obtained by Michael and J. P. Ryder by the condensation of chloral hydrate and orcinol. The formula assigned to the substance by Michael and Ryder was $C[C_6H_2(CH_3)(OH)_2]_3CH(OH)_2$. The authors find that on heating the aldehyd and phenol in aqueous solution at 100° for sixteen hours a colourless product is obtained, which melts at 252—263°, and has the formula $C_{16}H_{16}O_6$. The molecular weight, determined by raising the boiling-point of an alcoholic solution, was found to lie between 296 and 336. On heating in an atmosphere of coal-gas, the acid loses a molecule of water and is converted into an almost colourless lactone having the formula $C_{16}H_{14}O_5$. A triacetyl-derivative of the lactone is formed by heating the acid with excess of acetic anhydride. This derivative is colourless, and melts at 189°. On boiling the acid with excess of benzoyl chloride and pouring the hot solution into light petroleum, a tribenzoyl derivative of the lactone is obtained. The tribenzoate has the composition $C_{37}H_{26}O_8$, has no proper melting-point, is apparently insoluble in water, alcohol, and light petroleum, and when allowed to remain in dilute alcohol for some time, is converted into a dibenzoate of the acid which melts at 204°, is readily soluble in alcohol, and has the formula $C_{30}H_{24}O_8$.

56. "*Note on Hexamethylene and its Derivatives.*" By Emily C. Fortey, B.Sc.

In a preliminary note on hexanaphthene and its derivatives (*Proc.*, 1897, xiii., 161) it was stated that this hydrocarbon had been obtained from American light petroleum in a state of partial purity, and its identity with hexamethylene was pointed out. It has since been obtained by means of fractional distillation from Galician petroleum. The purest fraction boils almost constantly at 81·75°, and has a specific gravity of 0·7899 at 0°/0°. The following derivatives have been prepared:—*Monochlorhexamethylene*, $C_6H_{11}Cl$, was obtained by passing a current of dry chlorine into the liquid for some hours. It is a colourless liquid boiling at 141·3—141·6° under a pressure of 768 m.m., and has a specific gravity of 0·9991 at 0°/0°. *Dichlorhexamethylene*, $C_6H_{10}Cl_2$, was obtained together with mono- and a little tri-chlorhexamethylene by passing a rapid current of chlorine into heated hexamethylene. It is a colourless liquid when pure, but rapidly turns blue on exposure to air. It boils with slight decomposition at 194—195° under atmospheric pressure. Both mono- and di-chlorhexamethylene give a deep red colouration on warming with concentrated sulphuric acid. On heating dichlorhexamethylene with quinoline, a small quantity of a substance boiling between 80° and 90° is obtained, which appears to be dihydrobenzene. Its alcoholic solution gives a blue colouration with sulphuric acid (Baeyer, *Ber.*, 1893, xxvi., 230). Tetrahydrobenzene was obtained by heating monochlorhexamethylene with quinoline for seven or eight hours. It is a colourless liquid having the properties described by Baeyer (*l. c.*), and boils at 82·3° under a pressure of 764 m.m. *Monobromhexamethylene* could not be obtained by direct bromination of hexamethylene either with or without the aid of a bromine carrier. A small quantity was, however, prepared by the action of an aqueous solution of hydrobromic acid on tetrahydrobenzene. It is a colourless liquid which boils with slight decomposition at 162—163°. The present work will be continued with the view of preparing further derivatives of hexamethylene.

57. "*The Yellow Colouring Matter of the Leaves of Arctostaphylos uva ursi.*" By A. G. PERKIN.

Kawalier (*Jahr.*, 1852, 685) found the leaves to contain, besides gallic acid and arbutin, a glucoside ericolin, $C_{34}H_{56}O_{21}$, which yields on decomposition ericinol, $C_{10}H_{16}O$, and a sugar. More recently, B. Degraffe (*Am. Journ. Pharm.*, 1896, lxviii., 313) has identified the tannin as gallotannin. There is also present a yellow colouring matter of the composition $C_{15}H_{10}O_7$, crystallising in glistening yellow needles; this forms an acetyl-compound, $C_{13}H_5O_7Ac_5$, melting at 188—190°. On fusion with alkali, phloroglucinol and protocatechuic acid were formed. Though resembling quercetin in these points, it has the property of forming deep green solutions with dilute potassium hydrate. Regarding this reaction as due to impurity, the colouring matter was converted (*a*) into a sulphate, and (*b*) into an acetyl-derivative, and the colouring matter regenerated from these, but in each case it was unaltered in its behaviour towards alkaline solutions. Oxidation in alkaline solution did not destroy the green colouration until complete decomposition of the colouring matter had taken place. The presence of ellagic acid has also been detected, and thus besides gallotannin, ellagitannin is also present. Broach leaves contain the same colouring matter.

58. "*The Yellow Colouring Matters of various Adulterants of Sicilian Sumach.*" Part V. By A. G. PERKIN and P. J. WOOD.

This paper describes an investigation of the leaves of those plants which are employed for the adulteration of Sicilian sumach (*Rhus coriaria*). We are indebted for samples of these to Mr. P. Gennadius, Director of Agriculture in Cyprus.

The leaves of *Pistacia lentiscus* (shinia) contain a colouring matter of the formula $C_{15}H_{10}O_8$, forming an acetyl compound, $C_{15}H_4O_8Ac_6$, crystallising in colourless needles (m. p. 204—206°). As on decomposition this yields gallic acid and phloroglucinol, it is identical with myricetin, the colouring matter of *Rhus coriaria*. Two tannins appear to be present: one dissolves in ethylic acetate, yields gallic acid on decomposition, and is evidently gallotannic acid; the other is insoluble, and forms acetic acid, phloroglucinol, and gallic acid on fusion with alkali. When digested with dilute sulphuric acid, the latter yields a red product resembling the anhydrides of the catechol tannins. The further examination of this tannin is reserved. Shinia leaves contain 11·3 per cent of tannin, and appear to be a useful tanning agent, though not suitable for the same purposes as sumach.

The leaves and stems of *Tamaris gallica* and *T. africana* (bruca) contain the same colouring matter. It has the formula $C_{16}H_{12}O_7$, and forms an acetyl compound (m. p. 169—171°). Decomposition with alkali gave phloroglucinol and protocatechuic acid, and with hydriodic acid quercetin and a molecular proportion of methylic iodide were formed. This substance appears to be a new *methyl ether* of *quercetin*, distinguished from rhamnetin and isorhamnetin by its ready solubility in alcohol. So little of it was available for examination that its absolute purity could not be guaranteed. The tannin (8·4 per cent) is evidently a mixture of ellagitannin and gallotannin, for both ellagic and gallic acids were isolated as its decomposition products.

The leaves of the *Ailantus glandulosa* contain quercetin. The tannin present (11·9 per cent) is a mixture of ellagitannin and gallotannin, for both ellagic and gallic acids were isolated. This is a worthless tanning agent; the skin, though stained a deep colour, is practically untanned.

The colouring matter of the leaves of *Ficus carica*, the common fig tree, though resembling quercetin, could not be identified, as from 2 kilos. only 0·08 grm. of the substance was obtained. It is nearly devoid of tannin (analysis gave 1·6 per cent), skin being untanned though stained a dirty olive colour.

Gambuzzo, the stalks of the *Rhus coriaria*, contain a trace of myricetin and some gallotannic acid.

Broach leaves are employed in South Africa in place of sumach (*R. coriaria*), and are also replacing the Cape sumach (*Colpoon compressum*) (*Trans.*, 1897, lxxi., 1132). They contain 19·9 per cent of a catechol tannin, and they form a valuable tannin agent. The colouring matter, having the formula $C_{15}H_{10}O_7$, forms an acetyl compound, m. p. 188—190°, and on decomposition yields phloroglucinol and protocatechuic acid. It differs from quercetin in its reaction with dilute alkali, forming deep green solutions, and appears to be identical with the colouring matter of *Arctostaphylos uva ursi* (see preceding abstract).

The galls of *Pistacia terebinthus* contain a trace of myricetin, whereas Mangrove cutch (*Ceriops candolleana*) is devoid of yellow colouring matter.

59. "*The Hydrolysis of Starch by Acids.*" By HAROLD JOHNSON.

It has been generally believed that the hydrolysis of starch by acids is similar in character to that effected by diastase, except that the maltose, which is the final product of the action of diastase, is transformed by acids into dextrose. An examination of the products of acid hydrolysis shows, however, that these are not identical with those of diastase conversion, and that when starch is hydrolysed by dilute acids there is neither production of amyloins (molecular aggregates of maltose and the amylin group) nor of maltose. The nature of the products resulting from the reaction can be shortly described as follows:—

The cupric-reducing powers and the specific rotations of the intermediate substances (fractionated by means of alcohol) as well as those of the total products of conversion, can be expressed exactly in values of dextrose and the amylin group. The relation between the specific rotation and the cupric-reducing power is constant throughout the whole of the reaction, and, given one of these values, the other may be calculated by the equation $[\alpha]_{D\,3\cdot86}x^\circ = 195 - (195 - 52\cdot8)K_{3\cdot86}/100$, in which x = the specific rotation and K = the cupric-reducing power in terms of the percentage of dextrose.

The specific rotations of the intermediate substances (separated from the dextrose by precipitation with alcohol) vary between $[\alpha]_{D\,3\cdot86}$ 80° and 190°. It should be remembered that the intermediate compounds in diastase conversions have rotations which vary from $[\alpha]_{D\,3\cdot86}$ 190° to 150°, so that the substances from the acid conversions with rotations which fall as low as 80° must differ in character from those obtained by diastase.

The behaviour of the intermediate substances from the acid conversions, when submitted to dialysis, shows that they are definite compounds, and not mixtures of dextrose and other carbohydrates, as, after purification, they dialyse without undergoing a change in specific rotatory power. Moreover, they are unfermentable in the presence of Saaz and Apiculatus yeasts. When treated with phenylhydrazin acetate, they yield gummy precipitates, and on further hydrolysis with acids are completely transformed into dextrose. Their solubility in alcohol decreases as their specific rotation increases.

The products of acid conversion also differ in a marked degree from those of diastase conversion when submitted to the action of diastase. The fall in specific rotation in the case of the products of acid conversion is extremely limited at any time during the reaction. Thus the action of diastase on an acid conversion whose rotation has fallen to $[\alpha]_{D\,3\cdot86}$ 115° is nil. At 140° the fall is 5° or 6°. At 170° the fall is about 10°, the blue colouration produced by iodine disappearing at this point in the conversion under the influence of diastase. As, however, diastase has a slight degrading action on conversions which give no blue colourations with iodine, and have rotations between 140° and 115°, it is possible that an unreducing dextrin may be produced in the splitting up of the starch molecule; the slight fall in the rotation under the influence of diastase could then be explained by the degradation of this dextrin.

The action of dilute acids on starch can be expressed in its simplest form by the following equations:—

$$(C_{12}H_{20}O_{10})n + 2(H_2O)m = \left\{\begin{matrix}(C_{12}H_{20}O_{10})n-m \\ (C_6H_{12}O_6)m\end{matrix}\right. + (C_6H_{12}O_6)m,$$

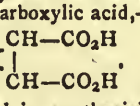
$$\left\{\begin{matrix}(C_{12}H_{20}O_{10})n-m \\ (C_6H_{12}O_6)m\end{matrix}\right. + (C_6H_{12}O_6)m + 2(H_2O)n-m = 2(C_6H_{12}O_6)n.$$

Taking into consideration their properties, the substances intermediate between starch and dextrose may be regarded as molecular aggregates of dextrose and the amylin group $(C_{12}H_{20}O_{10})n$; the name *gluco-amylins* will accurately describe them. Gluco-amylins with rotations of about $[\alpha]_D$ 3·86 80° or 90° have been recognised in commercial glucose under the name of gallisin.

The formation of gluco-amylins by acid hydrolysis is thus explained:—Acids, being able to hydrolyse free maltose, exercise this action also on the maltose in molecular aggregates, and therefore amyloins at the moment of their formation would be transformed into dextrose and gluco-amylins. The molecule of starch is probably formed by the condensation of a large number of molecules of dextrose. In the first place, two molecules of dextrose condense to form maltose, and then a large number of maltose molecules further condense to form starch.

60. "*Synthesis of Cis- and Trans-caronic Acid.*" By W. H. PERKIN, jun., and J. F. THORPE.

The cis- and trans-modifications of caronic acid were obtained by Baeyer (*Ber.*, 1896, xxix., 2796) by oxidising carone with alkaline permanganate, and as these acids when heated with hydrochloric acid yield terebinic acid, Baeyer concluded that they are the cis- and trans-forms of dimethyltrimethylenedicarboxylic acid,—



The authors have succeeded in synthesising these acids in a manner which proves that they have the constitution assigned to them by Baeyer.

When the anhydride of $\beta\beta$-dimethylglutaric acid is brominated and the product poured into ethylic or methylic alcohol, the following ethereal salts are easily obtained:—*Ethylic-α-bromodimethylglutarate*, $CO_2Et{\cdot}CHBr{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Et$, is a colourless liquid boiling constantly at 180° (30 m.m.); the corresponding *methylic salt* distils at 155° (22 m.m). The *acid ethylic salt* of α-bromodimethylglutaric acid, $CO_2H{\cdot}CHBr{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Et$, is a thick oil distilling without decomposition at 240° (35 m.m.). *Methylic-αα'-dibromodimethylglutarate*, $CO_2Me{\cdot}CHBr{\cdot}CMe_2{\cdot}CHBr{\cdot}CO_2Me$, is a colourless somewhat viscous liquid boiling at 172° (22 m.m.). The methylic and ethylic salts of α-bromodimethylglutaric acid and the acid ethereal salt above described, yield, on treatment with alcoholic potash, a mixture of acids which melts at 180—200°, and consists of a mixture of the cis- and trans-modifications of caronic acid. The two modifications may be separated by taking advantage of the difference in solubility of their ammonium salts in hot alcohol, as suggested by Baeyer. The sparingly soluble ammonium salt yields trans-caronic acid, which crystallises from water in lustrous prisms melting at 212°. This acid gives a sparingly soluble crystalline silver salt, but does not form an anhydride. From the readily soluble ammonium salt cis-caronic acid is obtained in plates melting at 174°, and yielding an anhydride melting at 54—56°. There can be no doubt that these acids are identical with the caronic acids prepared by Baeyer.

The authors are investigating the action of the bromo-ethereal salts described above on the sodium derivative of ethylic malonate.

61. "*Preparation of Solid Ammonium Cyanate.*" By JAMES WALKER and JOHN K. WOOD.

In connection with previous experiments on urea-formation (*Trans.*, 1895, lxvii., 746; 1897, lxxi., 489), it was thought desirable to make an attempt to prepare ammonium cyanate in the solid state. Liebig and Wöhler (*Ann. Phys. Chem.*, 1830, [ii.], xx., 393) by passing the vapour of cyanic acid into dry ammonia, obtained a product which they held to be a basic ammonium cyanate. From the description of their experiments, it appears likely that what they actually had in their hands was the normal ammonium cyanate mixed with considerable quantities of urea and of cyamelide. The reason why they did not succeed in preparing the normal cyanate in the pure state is that the heat of combination of the ammonia and the cyanic acid is so great that, under the conditions chosen by them, a large proportion of the ammonium cyanate was decomposed, with formation of the above impurities and of ammonia. If this heating is avoided, it is a matter of no great difficulty to prepare the cyanate in a state which nearly approaches purity. A solution of ammonia in anhydrous ether is gradually added to a solution of cyanic acid in anhydrous ether, both solutions being cooled to −20°. A gelatinous precipitate at once separates, which, after rapid filtration and removal of adhering ether, shrinks to friable masses of a pure white solid. If moisture is rigorously excluded during the operations, and the temperature never allowed to rise to the freezing-point, the product is practically pure ammonium cyanate. When freshly prepared, it dissolves in water without residue, yielding a solution which is neutral to litmus. This proves that the product is free from cyamelide and ammonia, and the only impurity to be feared is urea. The substance effervesces on treatment with nitric acid, and no urea nitrate separates. Silver nitrate solution produces a white precipitate, which is soluble in boiling water and separates out on cooling, thus exhibiting the properties of silver cyanate. Portions of the salt, on being analysed as soon after their preparation as possible, gave the following numbers, the cyanate radicle being estimated as silver cyanate.

	Found.	Theory for ammonium cyanate.
NH_4	30·0	30·0
CNO	70·9	70·0
N	46·8	46·7
C	19·8	20·0
H	7·0	6·7

The cyanate may be kept for a long time in closed tubes without undergoing any considerable alteration. Thus a portion which had remained at the ordinary temperature for fourteen days still contained over 95 per cent of cyanate. On heating in a melting-point capillary, the cyanate contracts visibly at a temperature somewhat above 60°, and melts suddenly at a temperature varying between 76° and 89°, according as the heating is conducted rapidly or not, and according to the tightness with which the material is packed. The fused mass, however, immediately solidifies, and does not again melt till a temperature of 128° is reached—urea melting at 132°. A minute quantity of gas is given off during the first fusion, and a litmus-paper introduced into the upper part of the tube is then turned blue. When the experiment is made on a larger scale, a smell of ammonia is perceptible. Corresponding to this liberation of ammonia, it is found that the transformed solid is not entirely soluble in water, a slight flocculent residue of cyanelide remaining. The first fusion observed when the substance is heated doubtless results from the rapid transformation of cyanate into urea, enough heat being evolved to liquefy the urea produced, which thereafter cools to a temperature below its melting-point. The contraction at first observed probably indicates the temperature at which the transformation proceeds at a perceptible rate. After five hours at 61°, a portion of the cyanate was found to be almost wholly transformed into urea, a small quantity of ammonia and

cyamelide being formed at the same time. Twenty hours' heating at 43° effected the transformation of only 28 per cent of the cyanate. On opening the tube, it was again found that ammonia had been produced, and that the residue was not completely soluble in boiling water. The transformation of the solid cyanate into urea seems, therefore, to be always accompanied by a subsidiary transformation into cyamelide and ammonia.

The investigation is being continued with a view to determining the accurate temperature of transformation of the cyanate, if this is possible, and also to effect the preparation of alkyl ammonium cyanates by similar means.

62. "*The Chlorine Derivatives of Pyridine.*" Part I. By WILLIAM J. SELL, M.A., F.I.C., and F. W. DOOTSON, M.A.

The authors have examined the action of phosphorus pentachloride on pyridine, and have isolated the following compounds: — (1) A dichloropyridine, m. p. 87—88°; (2) a trichloropyridine, m. p. 49—50°; (3) a trichloropyridine, m. p. 71—72°; (4) a trichloropyridine, m. p. 67—68°; (5) a tetrachloropyridine, m. p. 90—91°; (6) a tetrachloropyridine, m. p. 21—22°; (7) a tetrachloropyridine, m. p. 74—75°; (8) a pentachloropyridine, m. p. 123—124°.

63. "*Simple Experimental Illustration of the Law of Multiples.*" By A. WENTWORTH JONES, M.A.

Calculated quantities — for example, four times the milligrm.-molecules — of potassium chlorate and perchlorate are weighed into hard glass tubes provided with corks and delivery tubes, each passing by india-rubber connections through the hole in a beehive-shelf, to near the top of a graduated gas jar full of water in the pneumatic trough. After heating the tubes in the full Bunsen flame for a few minutes, gas ceases to come off, the flames are removed, and the tubes allowed to cool and to withdraw their original content of gas from the receivers through the upturned delivery tubes. The relative volumes collected stand, of course, in the proportion 3 : 4 for equal weights of residue in the tubes. In an experiment before a class, the volumes obtained were 146 and 194 c.c., *i. e.*, in the proportion of 3 : 4 almost exactly. After weighing tubes and residues, and then cleaning and weighing the tubes, the difference or weight of residue was, in each case, 0·30 grm.

64. "*Lauronolic Acid.*" By R. W. COLLINSON and W. H. PERKIN, jun.

In connection with the experiments made by one of the authors on isolauronolic acid, they have lately examined lauronolic acid with the following results.

Lauronolic acid is not reduced by sodium amalgam, but when treated with hydrobromic acid is converted into a hydrobromide, $C_9H_{15}O_2Br$, which melts at about 133° with decomposition, and when treated with bromine in chloroform solution, yields a substance which melts at 185° and seems to have the composition $C_9H_{13}O_2Br$.

Boiling with dilute nitric acid converts lauronolic acid into a substance of the formula $C_9N_{13}(NO_2)O_2$, which is volatile in steam, and melts at 170°.

When a cold solution of the sodium salt of lauronolic acid is oxidised with potassium permanganate, a syrupy acid of the formula $C_9H_{14}O_5$ is produced, which is at present under investigation.

Lauronolic acid, when warmed with sulphuric acid at 30—40°, is completely decomposed, carbon monoxide being formed together with substances which so far have not been investigated.

65. "*The Action of Aluminium Chloride on Camphoric Anhydride.*" By FREDERIC H. LEES and W. H. PERKIN, jun.

In the course of experiments on isolauronolic acid, on which one of the authors has been engaged for some years, an attempt was made to prepare this acid by a method described by G. Blanc (*C. R.*, 1896, cxxiii., 749—752, *Bull. Soc. Chim.*, 1896, [iii.], xv., 1191—1199), which consists in acting on a solution of camphoric anhydride in chloroform with aluminium chloride. For a long time the authors failed to obtain anything like the yield of isolauronolic acid obtained in this way by Blanc (40 per cent), and on investigating the cause of this discrepancy, they have isolated the following new substances as products of the reaction. (1) A *neutral oil* corresponding to about 30—40 per cent of the camphoric anhydride employed. This substance, which the authors propose to call *ψ-campholactone*, boils constantly at 163—164° (50 m.m.), has the formula $C_9H_{14}O_2$, and is isomeric with laurbnolic acid, isolauronolic acid, and campholactone. It is converted by treatment with potash into the corresponding hydroxy-acid, $C_8H_{14}(OH)CO_2H$, a thick syrup which readily loses water, reforming the lactone. When *ψ*-campholactone is heated with concentrated sulphuric acid at 90°, sulphur dioxide is evolved, and on adding water a crystalline acid is precipitated in quantity; this melts at 126°, and proves to be xylic acid, $C_6H_3Me_2CO_2H$ (1 : 3 : 4).

(2) An *acid* melting at 255—257°, which gives numbers on analysis agreeing with the formula $C_{11}H_{16}O_3$.

The authors are engaged in the examination of this acid and of *ψ*-campholactone, as they hope in this way to obtain results having a direct bearing on the constitution of camphoric acid.

66. "*On the Action of Bromacetal on the Sodium Derivative of Ethylic Malonate.*" By W. H. PERKIN, jun., and C. H. G. SPRANKLING.

For some months the authors have been engaged in the examination of this decomposition, and although their experiments are far from complete, they wish to give a short account of the results as yet obtained, in view of a recent paper by Harries (*Ber.*, 1898, xxxi., 37), which deals with substances somewhat similar to those obtained by them.

Bromacetal has little action on the sodium derivative of ethylic malonate at 100°, but when these substances are heated at 140—150° in sealed tubes, interaction takes place readily with the formation of ethylic acetalmalonate.

Ethylic acetalmalonate, $(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH(OEt)_2$, boils constantly at 151—154° (15 m.m.), and on hydrolysis with alcoholic potash yields the corresponding *acetalmalonic acid*, $(CO_2H)_2CH{\cdot}CH_2{\cdot}CH(OEt)_2$, a colourless syrup, which when heated with water at 190° is decomposed with elimination of carbon dioxide and alcohol, and formation of a substance which is apparently the half aldehyd of succinic acid, $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$. This is a colourless syrup, which on long standing deposits crystals, reduces Fehling's solution, combines with phenylhydrazine, and yields succinic acid on oxidation with nitric acid.

The authors are investigating these substances, as well as the action of bromacetal on the sodium derivatives of other ethereal salts.

67. "*The Sulphonation of Benzophenone and of Diphenylmethane.*" By ARTHUR LAPWORTH, D.Sc.

Benzophenone, as it contains the group —CO— in direct attachment to the benzene nucleus, should afford a considerable quantity of meta-acid on sulphonation. It has long been supposed that the major portion of the product was the para-disulphonic acid, as Städel obtained para-hydroxybenzoic acid on fusing it with alkali (*Ann.*, 1878, cxciv., 134). The author has been unable to confirm Städel's observation; the disulphonic acid he obtained by sulphonation yielded almost pure metahydroxybenzoic acid on fusion with alkali, and there is therefore no reason to regard the behaviour of benzophenone on sulphonation as exceptional. During the investigation the following substances were obtained and characterised. Benzophenonedisulphonic chloride, $C_{13}H_8O(SO_2Cl)_2$, crystallises from chloroform in large, anorthic plates melting at 138°, and the form described by Beckmann, melting at 121·5° could not be obtained. The *amide* forms needles melting

at 157°, and the *anilide* large crystals melting at 177—178°. The *piperidide* crystallises in monoclinic prisms or plates melting at 168°, and has the curious property of forming a transparent jelly when its alcoholic solution is slowly cooled. A brief study of the sulphonation products of diphenylmethane was made. They appear to be a mixture of disulphonic acids, of which one, doubtless the diparaacid, yields a *chloride*, $C_{13}H_{10}(SO_2Cl)_2$, melting at 124°, an *anilide* melting at 178°, and a *piperidide* melting at 171—172°. When the sulphonation is carried out by means of chlorosulphonic acid, *diphenylmethaneorthosulphone*, $C_{13}H_{10}SO_2$ is also produced; its constitution follows from the fact that, when oxidised, it yields the benzophenonesulphone described by Städel, the structure of which has been determined.

68. "*The Separation of Optical Isomerides.*" By Frederic Stanley Kipping and William Jackson Pope.

In a previous paper ("Racemism and Pseudoracemism," *Trans.*, 1897, lxxi., 989), the authors have dealt with a number of the properties of optically active compounds and their externally compensated isomerides. It would seem, however, that much may be learnt respecting the mutual relationships of these substances by a study of their respective behaviour towards solvents which are themselves optically active. In this preliminary note the authors record the results obtained up to the present in some experiments on the separation of a mixture of equal quantities of enantiomorphously related substances by crystallisation from optically active solvents. The first attempts which the authors made to effect such a separation were unsuccessful; inactive mandelic acid, for instance, crystallised unchanged from an aqueous solution of dextrose. Since, however, inactive mandelic acid is a well-defined racemic compound at ordinary temperatures, it might well be that the tendency to form a solid racemic compound would overcome any tendency towards separation due to the presence in the system of a third enantiomorphous substance; the authors were, therefore, led to attempt the separation of an externally compensated mixture of two substances which do not form a solid racemic compound at the temperature employed. These experiments were successful.

An externally compensated mixture of sodium ammonium dextro- and lævo-tartrate forms a solid racemic compound only above 27°, and when crystallised from water at ordinary temperatures crystals of the dextro- and lævo-isomerides separate in equal quantities side by side, and may be mechanically separated. The authors find, however, that when an optically inactive mixture of sodium ammonium dextro- and lævo-tartrates is dissolved in a concentrated aqueous solution of dextrose, and crystallisation allowed to take place spontaneously at ordinary temperatures (below 27°), the crystalline deposit which first separates contains a very considerable excess of the dextrorotatory salt; when freed from dextrose, first by re-crystallisation from water at ordinary temperatures, and then by fractional precipitation from a warm aqueous solution by alcohol, this first deposit yields a quantity of sodium ammonium tartrate having a high specific dextrorotation. Eleven samples of salt, each obtained from a different solution, have so far been examined; in only one case the salt separated by the method just described was optically inactive, whilst in all the others it was dextrorotatory. Full quantitative details will be published later, but to afford some idea of the extent to which separation occurs, the authors find that from 175 grms. of a crystallised optically inactive mixture of sodium ammonium dextro- and lævo-tartrates, treated as above in six separate and approximately equal portions, they obtained the following six samples of hydrated active salt:—

	1.	2.	3.	4.	5.	6.
Weight in grms.:—	3·2	3·8	3·0	3·7	4·2	3·5
$[\alpha_D]$	+15·50°	+22·07°	+22·97°	+23·30°	+20·65°	+10·56°

Landolt's value for the specific rotation of sodium ammonium dextro-tartrate calculated on the hydrated salt is $[\alpha]_D = 23·70°$. The authors have satisfied themselves that all the samples examined in the polarimeter were free from dextrose, and that the racemic acid used in making the salt was optically inactive. The results thus briefly recorded seem to show that enantiomorphously related substances are not equally soluble in presence of a third enantiomorphous substance; whether the difference under these conditions will be sufficient in all cases to render a separation of the two isomerides possible, thus adding another to the few methods by which this may be accomplished, is a matter which is still under investigation.

ROYAL INSTITUTION.

Annual Meeting, Monday, May 2, 1898.

Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

The Annual Report of the Committee of Visitors for the year 1897, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. Sixty-six new members were elected in 1897. Sixty-three lectures and nineteen evening discourses were delivered in 1897. The books and pamphlets presented in 1897 amounted to about 260 volumes, making, with 632 volumes (including periodicals bound) purchased by the Managers, a total of 892 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as officers for the ensuing year:—

President—The Duke of Northumberland, K.G.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir Frederick Bramwell, Bart.

Managers—Sir William Crookes, Sir Edward Frankland, The Right Hon. George Joachim Goschen, Donald William Charles Hood, David Edward Hughes, Alfred B. Kempe, Hugh Leonard, Sir William Huggins, Thomas John Maclagan, Ludwig Mond, Alexander Siemens, The Hon. Sir James Stirling, Sir Henry Thompson, Sir Richard Everard Webster, Sir William Henry White.

Visitors—Sir Alexander Richardson Binnie, Sir James Blyth, Bart., Charles Vernon Boys, Edward Dent, James Edmunds, Maures Horner, Edward Kraftmeier, Sir Francis Laking, T. Lambert Mears, Lachlan Mackintosh Rate, John Callander Ross, William James Russell, Sir James Vaughan, James Wimshurst, Alfred Fernandez Yarrow.

NOTICES OF BOOKS.

Commercial Fertilisers and Chemicals. By Dr. George F. Payne, State Chemist. Atlanta: G. W. Harrison. 1897. Pp. 116.

This Report refers more especially to the State of Georgia, where the author is State Chemist. It appears that Georgia stands a long way ahead of any other State in the quantity of artificial and chemical manures used, and the manufacture of fertilisers in that State has grown into a business of huge proportions. The two principal kinds here used are a simple acid phosphate, and a complete fertiliser made from acid phosphate, cotton-seed meal, blood, tankage or bone phosphate, nitrate of soda, kainit, and chlorate of potash: 15 to 16 per cent of avail-

able phosphoric acid is now obtained from a well-made acid phosphate from Charleston rock,—a very good proportion.

The number of analyses of fertilisers made during the season 1896-97 was 6015, against 4880 in the season before.

The total number of tons of commercial fertilisers used in the United States during 1896 was over 1,500,000, of which over 1,100,000 tons was used in the South-eastern group of States, among which Georgia stands at the head with a record of 335,617 tons, or more than one-fifth of the whole lot together. A new insecticide is described called "grey mineral ash," which is said to be superior to and safer than Paris green; it consists of certain proportions of sulphate, sulphide, and hydrate of barium, carbon, water, and silica; when mixed with water and applied to the crops, the effect is to give off sulphuretted hydrogen. A number of notes in reply to various enquiries that have been made are given, and the report finishes with a large number of tables of the complete analysis of all the different brands of commercial fertilisers used.

The Freezing-point, Boiling-point, and Conductivity Methods. By HARRY C. JONES. Easton, Pa.: Chemical Publishing Company. 1897. Pp. 64.

IT has long been known that the freezing-point of a solution of any substance is lower than that of the solvent used. Raoult tried to generalise it thus:—That "one molecule of any complex substance dissolved in 100 molecules of a liquid, lowers the freezing-point of the liquid by nearly a constant amount, which is 0·62. This has been shown not to hold rigidly." The author then goes on to discuss the variations from this rule, and gives some interesting facts concerning them. The results found with water as a solvent are entirely different to those obtained when benzene, or acetic, formic, or benzoic acid is the medium employed. Compounds like the non-electrolytes give a very nearly constant figure with water, approximately 18·8.

The application of the freezing-point method to the determination of molecular weights in solution is described, using Beckmann's apparatus; after which the same method for the measurement of electrolytic dissociation is considered; an ion lowers the freezing-point of a solvent just as much as a molecule, and, if a molecule dissociates into two ions, the freezing-point of a given amount of a solvent will be lowered just twice as much as if it is not dissociated. Thus it is possible for any given dilution to determine the amount to which an electrolyte is dissociated.

Part II. is on the boiling-point method, and it is stated as a well-known preliminary that "the presence of a foreign non-volatile substance diminishes the vapour-pressure of the solvent," and hence raises the boiling-point; there are thus two quantities to measure. The application of the boiling-point method to the determination of molecular weights in solutions is not so delicate as the freezing-point method, as it is very sensitive to barometric changes: a number of forms of apparatus have been devised by Beckmann, by Hite, and by the present author, but we cannot describe them without the diagrams. The conductivity method is described in Part III., and its application to the method of electrolytic dissociation is also here given. The great drawback to electrolytic methods is, that after a continuous current has passed for a short time, the electrodes become polarised, *i.e.*, covered with gas; several devices have been tried to overcome this, but the simplest is to use an alternating current; several methods of effecting the determination are illustrated, and full details given for carrying out the measurements.

The book is a most interesting one, well and clearly written, and printed in clear type, but—and there is always a but—there is no index.

Organic Chemistry for the Laboratory. By W. A. NOYES, Ph.D. Easton, Pa.: Chemical Publishing Company. 1897. Pp. 257.

A MOST important remark, made by the author in his Preface, is that "a satisfactory working knowledge of organic chemistry cannot be acquired without the ability to use German books." We may add that a successful student must also be able to follow the flood of original work which is being published, not only in German but other Continental languages, besides what is done in England. The author has divided the subject into ten principal headings, but he seems to begin rather abruptly with the idea that the student has already a fairly good knowledge of the subject, though there is nothing in the title to indicate that the book is intended for advanced students only.

There is no necessity to analyse the book closely, as the general outline of the system on which organic chemistry is built up is so well known; suffice it to say that the subject is well and clearly explained, with numerous references to original papers throughout. The Index is very complete, and comprises sixteen pages.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 13, March 28, 1898.

Use of Chloride of Palladium for the Detection of small quantities of Carbonic Oxide in the Air, and on the Conversion of this Gas into Carbonic Acid at the Ordinary Temperature.—MM. Potain and Drouin.—The presence of carbonic oxide in the air, even when in very small quantities, can easily be detected by passing the vitiated air in very fine bubbles through a dilute solution of chloride of palladium. Ten c.c. of a solution containing 1 m.grm. of the chloride, acidulated with two drops of hydrochloric acid, are placed in a special flask, through which the air can be drawn; when the apparatus is started, no matter how small a quantity of carbonic oxide is present, the chloride is decomposed, and the palladium is deposited in a blackish film on the sides of the tube. This deposit points to the presence of a reducing agent. The proportion of the gas present can be estimated by colorimetric means, by comparing the colour of a solution which has been tested with that of a similar solution of known strength which has not been so treated. The authors do not claim great chemical accuracy for this new method, but they think it will be of great service from the hygienic point of view on account of its speed.

On an Iodide of Tungsten.—E. Defacqz.—(See p. 204).

Quinoleic Bases.—Marcel Delépine.—The author has studied some quinoleic bases from the thermochemical point of view, in order to determine the thermic variations which accompany their formation, which, as is well known, is generally by the action of an aldehyd, an acetone, or similar substances able to give rise to these functions, on a primary aromatic amine more or less complex. As we have not much knowledge on the subject the author has at present confined his researches to quinolein, quinaldine, and their tetrahydrides. Experiments were made with quinolein from tar, and also the same prepared synthetically, with tetrahydroxyquinolein, quinaldine or α-methylquinolein, and tetrahydroquinaldine; these experiments are fully described and commented on, the general conclusions being that the heat of formation is very small, though this may be accounted for by that absorbed by the

water of formation, and other reasons, such as possible polymerisation, &c.

Combination of Organic Bases with various Oxygenated Salts.—D. Tombeck.—It has already been shown that aniline and its derivatives, such as the bases of the pyridic series, are able, like ammonia, to combine with the haloid salts of zinc and cadmium, giving well-crystallised bodies, of which the author has already described the compositions and properties. He now finds that compounds analogous to those used before give corresponding compounds with nickel, cobalt, magnesium, and manganese salts under conditions but slightly different. Aniline again, like ammonia, combines with several oxygenated salts. The general method for the preparation of the compounds formed in this case consists of pouring an excess of aniline into a solution of the metallic oxygenated salt; on agitation the crystalline precipitate is formed.

Zeitschrift für Anorganische Chemie,
Vol. xvi., Nos. 2 and 3.

The Combustion of Organic Substances in Aqueous Solution.—I. K. Phelps.—By oxidation with $KMnO_4$ the amount of CO_2 obtained from ammonium oxalate, barium formate, and acid potassium tartrate is accurately determined by absorption in standard $Ba(OH)_2$ solution and titration of the excess of $Ba(OH)_2$. Chromic acid gives also fairly good results as oxidiser with ammonium oxalate and cane-sugar. The amount of oxygen in some compounds can also be determined by using a known quantity of chromic acid, but the method is cumbrous.

Titration of Sodium Thiosulphate by Iodic Acid.—Claude F. Walker.—Riegler's method of titrating thiosulphate with HIO_3 is shown to be very inaccurate, as the end point varies greatly with the volume of the solution, and the nature of the reaction cannot be expressed by any simple chemical equation.

The Constitution of Inorganic Compounds.—Alfred Werner.—Complex cobalt ammonium salts were investigated and carefully analysed. The sulphate had the formula $Co_2(NH_3)_8(OH)_2(SO_4)_2 3H_2O$ assigned to it. Other salts were also examined, chiefly (1) oxy-di-imido-octammindicobalt salts, of which the chloride, bromide, sulphate, and nitrate were prepared and examined, and the formula—

$$O\begin{Bmatrix} NH:Co_2(NH_3)_8 \\ NH:Co_2(NH_3)_8 \end{Bmatrix} Cl_8 + 6aq.$$

assigned to the chloride. (2) Hydrosulphimide-octammindicobalt salts, of which the nitrate, sulphate, bromide, iodide, &c., were prepared, and the formula—

$$HN:Co_2\begin{Bmatrix} SO_4H \\ (NH_3)_4 \end{Bmatrix}(NO_3)_3$$

was given to the nitrate.

A New Determination of the Atomic Weight of Nickel.—T. W. Richards and A. S. Cushman.—Already inserted.

Constitution of Cobalt, Nickel, and Rhodium Bases.—S. M. Jörgensen.—There appears to be a difference in the constitution of complex salts of cobalt and chromium. To investigate this difference the author prepares basic diquotetrammoncobalt sulphate—

$$\begin{matrix} OH_2OH_2 \\ Co(NH_3)_4SO_4 \\ OH_2 \end{matrix}$$

chloride, and nitrate, and compares these with the corresponding salts of chromium. He suggests that the difference may be explained by the constitutional formula—

$$Cl(NH_3)_2(OH)_2\!>\!Co.O.Co\!<\!(NH_3)_4Cl \quad (HO,\ Cl)$$

for cobalt, and—

$$Cl(NH_3)_2(OH)_2\!>\!Cr.O.Cr\!<\!(NH_3)_4Cl \quad (Cl,\ OH)$$

for the corresponding chromium salt.

Electrolysis of Hydrochloric Acid.—F. Haber and S. Grinberg.—The substances formed at the anode and cathode were investigated with acid solution of various strengths, and the following results obtained. Chlorine is evolved at the anode, when the acid is concentrated, with a yield of 100 per cent; and the yield decreases as the acid is diluted. Hypochlorous acid is present in traces in the anode gas when dilute acid is electrolysed. Acid solutions of strengths between normal and $\frac{1}{10}$th normal give chloric acid, which is accompanied by a small quantity of H_2O_2. Perchloric acid is present in dilute acid solution. Oxygen is evolved by the electrolysis of dilute acid, and forms about 50 per cent of the anode gas.

Chemiker Zeitung.
1898, No. 25.

Study of Aluminium as a Reducing Agent.—Léon Franck.—Aluminium powder contains small quantities of silica and iron, which must be carefully estimated when aluminium is used as a reducing agent. The author shows that about 0·8 per cent of silica and about 0·34 per cent of iron are present in the purest forms of commercial aluminium powder. He then investigates the reducing properties of aluminium. (1) Phosphorus combines in various proportions with aluminium:—Al_7P_3, obtained as a greyish black infusible mass; Al_5P_3 as a yellowish grey infusible mass; an unestimated compound forming little dark blue needles; and Al_3P and 2(AlP) as balls of metallic appearance. All these compounds are decomposed by water with evolution of PH_3. (2) Aluminium decomposes phosphates at a high temperature, with formation of phosphorus. By the addition of some silicic acid the decomposition is almost quantitative and according to the equations—

$$6NaPO_3 + 10Al + 3SiO_2 = 3Na_2SiO_3 + 5Al_2O_3 + 6P,$$
$$3Ca(PO_3)_2 + 10Al + 3SiO_2 = 3CaSiO_3 + 5Al_2O_3 + 6P.$$

By means of this reaction a new method of estimating phosphorus is described. (3) Aluminium decomposes CO_2 according to the equation $3CO_2 + 4Al = 2Al_2O_3 + 3C$; CO according to the equation $3CO + 2Al = Al_2O_3 + 3C$; and carbonates according to the equations—

$$Na_2CO_3 + 2Al = Al_2O_3 + C + NO_2,$$
$$CaCO_3 + 2Al = Al_2O_3 + C + Ca$$

During all these reactions some aluminium carbide is formed. (4) Aluminium is both a good and a sure reducing agent; for it decomposes metallic oxides, forming the metal and Al_2O_3; it decomposes sulphates forming sulphur and sulphides, and chlorides forming the metal. (5) A mixture of aluminium powder and sodium peroxide moistened with some water burns spontaneously, with dazzling light.

MISCELLANEOUS.

New York Agricultural Experiment Station, Geneva, N.Y.—The Director of this Experiment Station, Mr. W. H. Jordan, appears to have been doing good and useful work during the past year. Twenty-nine bulletins have been issued during the year on all sorts of subjects connected with or relating to agriculture. These bulletins are widely circulated among the farmers of the State, and carefully prepared abstracts are printed in the news and agricultural papers.

Sanitary Institute. — Sir Joseph Fayrer, Bart., K.C.S.I., M.D., LL.D., F.R.S., has accepted the Presidency of the Seventeenth Congress of the Sanitary Institute, to be held in Birmingham, commencing September 27th.

American Association for the Advancement of Science. — The fiftieth Anniversary Meeting of the American Association for the Advancement of Science will, we are informed, be held in Boston during the week beginning Monday, August 22, 1898. Full particulars can be obtained from Mr. A. Lawrence Rotch, Secretary, Boston, U.S.A.

A Natural Silicic Ether. — E. Drechsel. — By exhausting ordinary white bedding feathers with warm ether, in an extraction apparatus, and leaving the etherised extract to cool, M. Drechsel has obtained a substance, fusible at 52°, easily soluble in chloroform, very slightly soluble in alcohol, and soluble in ether. On analysis it gives figures corresponding to the formula $Si(OC_{34}H_{59}O)_4$. This substance may thus be the ortho-silicic ether of a bivalent alcohol, $C_{34}H_{60}O_2$, a homologue of cholesterine. The author has tried to prepare a homologous ether from a solution of chloride of silicium in chloroform and cholesterine; he obtained a body with analogous properties, melting at 59°. This ether, obtained from feathers, is the first organic compound containing silicic acid met with in nature.—*Centralblatt fur Physiol.*, vol. ii., p. 361.

Third International Congress of Applied Chemistry, Vienna, 1898. — 1. The third International Congress of Applied Chemistry will be held on the 28th of July, 1898, in Vienna, and will last until August 2nd, inclusive.

2. The subjects of the Congress are as follows:—

a. Consultations concerning important questions in all departments of applied chemistry, and particularly of those the solution of which is a matter of public interest.

b. Agreement upon methods to be considered internationally valid for the analysis of such products as are valued upon the basis of their chemical composition.

c. Agreement upon methods to be considered internationally valid for the use of the different chemical industries.

d. Discussion on questions of instruction in applied chemistry, and consultations upon general affairs of chemists. And—

e. Commencement of a friendly understanding between the representatives of the different departments of applied chemistry at home and abroad.

3. For the settlement of the work of the Congress there will be two general meetings and a further number of special consultations. Besides these there will be excursions for the purpose of visiting Scientific Institutions and Establishments.

4. The special consultations of the Congress will be divided into twelve Sections, as follows:—

I. General analytical chemistry and chemical instruments (general methods of analysis, analytical apparatus, measuring instruments, hydrometers, &c.).

II. Chemistry of food, medical and pharmaceutical chemistry. (The chemical and physical analysis of foods, discussions on chemical questions regarding foods in trades which do not come under the head of any other section; further questions of medical and pharmaceutical chemistry.

III. Agricultural chemistry. (Analysis of dairy products).

IV. Sugar industry, starch and grape sugar manufacture.

V. Zymology:—

1. Subsection. Brewing and malting.
2. Subsection. Alcohol and yeast industry.

VI. Oenochemistry.

VII. Chemical industry of inorganic substances. (Sulphuric acid. Soda and chloride of lime manufacture, alkali industry, artificial manure making, lime and cement industry, industry of illuminants, glass, china and earthenware manufacture).

VIII. Metallurgy and the manufacture of explosives.

IX. Chemical industry of organic substances. (Aniline dyes, dyeing and printing, manufacture of pharmaceutical preparations, chemistry of fats, oils, and lubricants, paper and xylonite industry, tanning, and glue manufacture).

X. Chemistry of the graphic industry. (Photo-chemistry, photographic and chemical printing, colour-printing).

XI. Questions of instruction and the general affairs of chemists.

XII. Electro-chemistry.

Papers to be read at the meeting should be in the hands of the General Secretary, M. F. Strohner, Vienna IV/2, Schönburgstrasse 6, not later than the 1st of June. It is requested that no paper be longer than 5 pages 8vo in print.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Royal Institution, 5. (General Monthly Meeting).
—— Society of Arts, 8. (Cantor Lectures). "Electric Traction," by Prof. Carus Wilson.

TUESDAY, 10th.—Society of Arts, 4.30. "The Art of William Morris," by F. S. Ellis.
—— Royal Institution, 3. "The Historical Development of Europe," by Samuel Rawson Gardiner, M.A., D.C.L., LL.D.

WEDNESDAY, 11th.—Society of Arts, 8. "Water Gas and its Applications," by Prof. Vivian B. Lewes.

THURSDAY, 12th.—Royal Institution, 3. "Heat," by The Right Hon. Lord Rayleigh, F.R.S., &c.

FRIDAY, 13th.—Royal Institution, 9. "Recent Experiments on certain of the Chemical Elements in relation to Heat," by Prof. W. A. Tilden, D.Sc., F.R.S.
—— Physical, 5. "Galvanometers," by Prof. W. E. Ayrton and T. Mather.

SATURDAY, 14th.—Royal Institution, 3. "Programme Music" (with Musical Illustrations), by Sir Walter Parratt, Mus. Doc., Master of the Queen's Music.

THE
ARRANGEMENT OF ATOMS IN SPACE.
By J. H. VAN 'T HOFF.
Second, Revised, and Enlarged Edition.
With a Preface by JOHANNES WISLICENUS, Professor of Chemistry at the University of Leipzig;
and an Appendix, 'Stereochemistry among Inorganic Substances,' by ALFRED WERNER, Professor of Chemistry at the University of Zurich.
Translated and Edited by ARNOLD EILOART.
LONDON, NEW YORK, and BOMBAY:
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INSTITUTE of CHEMISTRY of GREAT BRITAIN and IRELAND.
Founded 1877. Incorporated by Royal Charter, 1885.
EXAMINATIONS for the FELLOWSHIP (F.I.C.) and ASSOCIATESHIP (A.I.C.) will be held at the Laboratories of the Institute on Tuesday, the 12th day of July, 1898, and three following days.
In the event of 40 Candidates presenting themselves, those for Final Examination will be examined from Tuesday, 19th, to Friday, 22nd July.
Forms of application and an outline of the regulations can be obtained from the Secretary.
Full particulars are given in the "Book of Regulations for Admission to the Membership and Register of the Members and Students," to be obtained on application to Messrs. Blundell, Taylor, and Co., No. 173, Upper Thames Street, London, E.C. Price 1s., post free.
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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2007.

KOPFER'S METHOD FOR THE DETERMINATION OF CARBON AND HYDROGEN.

By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER.

Having had occasion recently to try some of the methods of determining carbon and hydrogen which have been proposed from time to time as alternatives to those in common use, we believe that the results which we have obtained may be of sufficient importance to those who are interested in organic analysis to justify their publication.

Of the methods which have been proposed to replace the ordinary method of combustion with copper oxide, that devised by Kopfer (*Zeitschrift fur Anal. Chemie*, 1878, xvii., 1) is perhaps best known. It is described at considerable length in such recent works as Vortmann's "Anleitung zur Chemischen Analyse Organischer Stoffe," and in Meyer and Jacobsen's "Lehrbuch der Organischen Chemie" (1893) it is referred to as a method which has been favourably criticised in many quarters.

Great advantages are claimed for this method by its author, of which the most important are that the combustion-tube may be much shorter than that usually employed; that the amount of gas consumed is less, and the time occupied in the operation shorter. It is further claimed for the method that it gives more accurate results for hydrogen, and that it is applicable to all classes of organic bodies. The results given by the author for substances differing so widely from one another in character as naphthalene, para-dichlorbenzene, nitro-benzene, and allyl-mustard oil, leave, *as a rule*, nothing to be desired in point of accuracy.

In view of the manifest advantages supposed to belong to this method, it seemed to us somewhat surprising that it had not come more generally into use. With the view of testing its capabilities, we made a series of determinations, following as closely as possible the directions given in the original paper.

The combustion is carried out in a hard glass tube 40 to 50 c.m. long and from 13 to 15 m.m. wide, which is drawn out at one end to about 4 m.m. diameter.

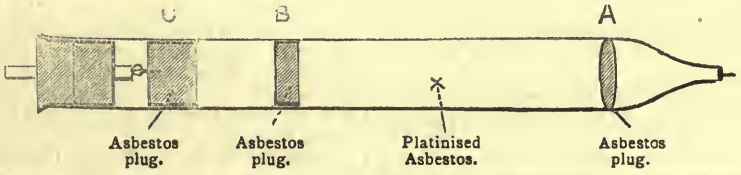
A plug of asbestos, A, covered with thin platinum foil, is placed in the drawn out end of the tube, and behind this from 20 to 25 c.m. of the tube are fitted with platinised asbestos held in position by a second plug, B, which ought not, however, to fit the tube too tightly. A third plug, C, is necessary, which ought to be cylindrical and to fit the tube properly, and be provided with a loop of platinum wire, so that it may be conveniently drawn out and in. The whole tube is placed in a furnace of special construction, provided with four fixed burners in the front part and with a movable burner behind, and that part of the tube which contains the platinised asbestos is wrapped in three or four plies of iron or copper wire gauze, in order to protect it from the gas flames. The tube, before being used, is moderately ignited in a current of oxygen for half an hour. It is then allowed to cool, the absorption apparatus attached, and the boat containing the substance introduced into the part of the tube lying beween the plugs B and C. A slow stream of oxygen is now passed through the tube, which is then heated, beginning with the three front jets under the layer of platinised asbestos, the flames being so regulated that, at the most, they are 4 c.m. in height. After some minutes the back movable burner is also lighted and placed under the plug C. The flame may be large, and may reach 2 c.m. over the tube. The movable flame is gradually brought nearer to the substance, whereby the progress of the combustion, which can be observed by the gas-bubbles passing through the potash solution, can be regulated, Lastly, the fourth gas burner under the front part of the tube is also lighted, and the operation brought to an end in the same way as in an ordinary combustion.

The platinised asbestos used is prepared by shaking up platinum-black with woolly asbestos.

The process requires to be modified when other elements besides carbon, hydrogen, and oxygen are present.

Kopfer gives numerous results obtained by his method. With cane-sugar he found, in two experiments, results agreeing perfectly with the calculated quantities, each combustion taking only one hour. With styracine, a body containing a high percentage of carbon, three analyses gave results agreeing with one another and with the theoretical numbers. Each combustion in this case occupied one and a half hours.

For substances which are volatile without decomposition an additional layer of platinised asbestos, 50 c m. long, has to be employed. With this additional layer, and some slight modification of the manipulation, Kopfer succeeded in obtaining excellent results with such substances as naphthalene, toluene, and xylene; each combustion occupied from 1¼ to 1½ hours.



In dealing with bodies containing nitrogen a longer tube—about 60 c.m.—is employed, and a layer of granular lead peroxide is placed in the front part of the tube, which is kept at a temperature of 180 to 200° C. during the combustion. The analysis of nitro-benzene performed in this way also gave satisfactory results.

In the analyses which we carrried out by this method every care was taken to follow closely Kopfer's directions, and to employ the various precautions which he indicates as necessary in the case of certain classes of substances. In order to secure the most favourable conditions for complete combustion, we prepared the platinum-black by Loew's method (*Berichte*, xxiii., 289 *a*), which is considered to yield this substance in a very active condition.

Our first experiments were made with easily combustible substances, and after a little practice we obtained fairly accurate results. The following numbers were obtained with cane-sugar:—

I. 0·2058 grm. gave—
0·1168 grm. H_2O = 6·30 per cent hydrogen.
0·3153 grm. CO_2 = 41·78 „ carbon.

II. 0·2190 grm. gave—
0·1220 grm. H_2O = 6·18 per cent hydrogen.
0·3335 grm. CO_2 = 41·53 „ carbon.

	Found.		Calculated.
Carbon ..	41·78 p.c.	41·53 p.c.	42·10 p.c.
Hydrogen..	6·30 „	6·18 „	6·44 „

Time occupied in both cases about one hour.

With volatile bodies we were less fortunate; with ethyl alcohol and benzene we failed altogether to obtain results even approximately correct.

As a nitrogenous body not difficult to burn we selected urea; the combustion was carried out with the modifications indicated above. We obtained the following results:—

0·2085 grm. gave—

0·1210 grm. H_2O = 6·46 per cent hydrogen.

0·1492 grm. CO_2 = 19·51 „ carbon.

	Found.	Calculated.
Carbon .. =	19·51 p.c.	20·00 p.c.
Hydrogen.. =	6·44 „	6·66 „

With substances containing a large percentage of carbon the results were altogether discouraging. Cinchonine and corybulbine (one of the alkaloids of *Corydalis cava*) were analysed, but the results were invariably low.

After spending much time and trouble over the method, and after performing a large number of experiments, of which we have not thought it worth while to quote more than a few, we came to the conclusion that the method is useless as a general method for the determination of carbon and hydrogen. With substances which are non-volatile and easily burned, it can be made to yield fairly accurate results. In the case of volatile substances we believe it to be altogether inapplicable, the difficulty of so regulating the rate of combustion as to prevent any of the material from volatilising undecomposed into the absorption apparatus being insuperable. It is well known that by the usual methods it is occasionally extremely difficult to effect complete combustion of some of the alkaloids. We had hoped to find this method applicable to such cases on account of the energetic oxidising action attributed to the platinum-black. As a matter of fact, we found it inferior to the ordinary method, the results being invariably too low. Others who have attempted to apply the method to such substances have also found it wanting. Zeisel, in a paper on Colchicin (*Monatshefte*, vii., 1886, p. 557), obtained results which were too low both for carbon and hydrogen.

We do not mean to assert that we have demonstrated that the method is absolutely incapable of yielding accurate results except with easily combustible bodies like cane-sugar and urea. If, however, it is capable of a more general application, our experience shows that the conditions for success would have to be specially studied in each case. A good practical method for determining carbon and hydrogen should be applicable with very slight modification to all the cases that may arise, and this condition is admirably fulfilled by the copper oxide method as usually practised. Since Kopfer's method does not fulfil this condition, it is manifestly of little practical value to the organic chemist.

We have also investigated some of the other methods which have been proposed for the estimation of carbon and hydrogen, especially Lippmann and Fleissner's method with copper oxide asbestos, and hope to communicate the results in a future paper.

University College of North Wales, Bangor.
April 15, 1898.

CRYSTALLISED CARBON DIOXIDE.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, New South Wales.

When solid carbon-dioxide is examined under the microscope it presents along its edges projecting wire-like crystals, which have branching filaments issuing from them, apparently at right angles, resembling somewhat the groups of minute crystals seen in crystallised iron, gold, and ammonium chloride.

The rapidity with which the carbon-dioxide evaporates makes it difficult to catch the form of the crystals, either by photography or other means.—*Proc. Australasian Assoc. for the Advancement of Science.*

LIQUEFACTION OF HYDROGEN AND HELIUM.

On Thursday, the 12th inst., Professor Dewar gave to the Royal Society an account of the results of recent low temperature research, which have culminated during the last day or so in the successful liquefaction of hydrogen and helium. About 20 cubic centimetres of clear colourless liquid hydrogen were obtained, and its properties and reactions examined.

SEPARATIONS FROM CHROMIC ACID.

IV. The Separation of Chromium, and A Reply to Mr. Galbraith's Criticisms.

By HARRY BREARLEY.

The reaction between potassium chromate and a neutral chromic salt has been so frequently observed, and analyses of the resulting precipitate so often recorded, that the fact of its existence needs only to be casually mentioned. The reaction, expressed in a manner analogous to the preceding ones, is very fully dealt with in Storer and Eliot's papers (Chem. News, vi., 121).

The bearing of this reaction on the quantitative separation of the salts of chromic oxide from chromic acid is just as important here as in the like separation of iron or aluminium. In practice, however, the former separation is so rarely necessary that one seeks almost in vain for an account of processes in which to note possible interferences.

In making the final analyses of the precipitated $Cr_2O_3{\cdot}CrO_3$, Storer and Eliot made use of a method by Vogel (Fresenius, "Quant. Anal.," p. 294), but the preliminary analyses were effected by dissolving the precipitate in nitric acid and separating the chromic oxide with a faint excess of ammonia. Separations by these means of the usual amount of potassium chromate from half a grm. of chromium (as Cr_2Cl_6) showed that (using fractional filtration) as little as 50 per cent of the chromic acid might be in the filtrate, the deficiency being presumably due to the formation of $Cr_2O_3{\cdot}CrO_3$, or a more basic chromate. Storer and Eliot remark that the precipitate obtained in this way is brownish green in colour, but after thorough washing assumes the common appearance of chromic oxide. Without commenting on the worthlessness of the colour as an indication of purity, or on the fact that Storer and Eliot repeatedly note the impracticability of completely decomposing $Cr_2O_3{\cdot}CrO_3$ by washing, is it not strange that when this method of analysing the precipitate comes to be abandoned there should be urged against it such comparatively insignificant errors as the solubility of the chromic hydrate in the excess of ammonia, whilst the error due to the formation of $x Cr_2O_3{\cdot}y CrO_3$ should be entirely overlooked?—another striking instance of the assumption that a compound so feeble as to be decomposed by washing must needs be completely resolved by an excess of an energetic precipitant.

Failing to meet with already described methods of precipitating the chromic chloride from the potassium chromate, it seemed interesting to observe with what success some common methods of precipitating chromic salts from pure solution could be applied to this separation. As these observations were very much in line with those already illustrated in preceding separations, it will suffice to state the conclusions in general terms.

Separation with Soda Hydrate.

With this reagent in slight excess, and the mixture merely raised to boiling, there was an approximate perfect separation. The prolonged boiling, which is necessary

to re-precipitate small amounts of chromic hydrate, is decidedly an advantageous operation. It transforms the separation into a perfectly accurate one. Larger amounts of soda precipitate the chromic hydrate free from chromic acid without prolonged boiling, but they are inadmissible on account of the solubility of the precipitate in an excess of the precipitant.

Separation with Soda Phosphate.

This reagent may be applied in two or three ways. First alone, in which case—presuming that there is free acid to be neutralised—it becomes interesting to note that the salts of chromium, like those of iron and aluminium, but in a less degree, are able to dissolve their own hydrate, and roughly indicate the point at which they begin to do so by changing to an olive-green colour. If to a solution thus neutralised a small excess only of soda phosphate be added, the results are 1 or 2 per cent too low, a deficiency which may be amended by adding larger excesses. From a faintly acid solution the chromic acid is perfectly separated by adding soda phosphate and soda acetate, and boiling ("Select Methods," p. 127). It is noticeable in these cases that when the precipitate forms in the cold it is frequently dark-coloured, but changes to the accustomed green as the temperature rises. This would seem to supply a reason for maintaining the solution at boiling-point for a while, and to indicate that the reagents had best be added to the hot solution. The phosphate may be added to an acid solution, and then caused to precipitate the chromium by making the solution alkaline. A slight excess of ammonia along with minimum amounts of phosphate will not do,—one or the other reagent must be decidedly in excess. Soda along with soda phosphate gives excellent results. Other methods in which the chromic acid is precipitated have not been observed.

Oxidising Reagents.

Chromium salts are frequently used to illustrate the powers of a new oxidising agent, and so it happens that a longer list of substances than may be appropriately named are said to be capable of oxidising chromic oxide to chromic acid; yet, strangely enough, a great number of these reagents are elsewhere said to partly fail when applied to such a purpose. The anomaly seems to be explained by the fact that the conditions under which the best results can be obtained are empirical ones, and may be easily missed in a casual test. Such, at least, has been my experience. Without attempting to state the order in which the oxidising reagents are to be preferred for this purpose, it will serve to illustrate the empirical nature of the general reaction if I carefully examine one reagent. I have chosen—

Permanganate in Acid Solutions,

under which head may be included the freshly precipitated manganese dioxide.

The oxidising effect of permanganate is not immediate, but gradual, and the last portions of the chromic oxide strongly resist the attacks of small excess of permanganate, or rather of the dioxide got from the decomposed permanganate. Thus, working on 25 c.c. of reduced chromate, we may recover after boiling for—

5	10	30	60 minutes,
21·1	21·9	23·3	23·9 c.c.

of the added chromate, and it would seem to be possible to complete the oxidation by boiling long enough. I have oxidised 49·7 c.c. out of 50 c.c. of reduced K_2CrO_4, when the permanganate, being added from a burette, was never more than a few drops in excess (permanganate = 25 grs. per litre).

The acidity (H_2SO_4) of the solutions is another factor. Increasing acidity favours the oxidation, but this modification cannot be worked very far, because, according to Leffler (Chem. News., lxxvii., 156), the precipitated manganese oxides become partly dissolved without being completely decomposed, and are thus able to augment the measured oxidising effect of the chromic acid, and further (Arnold, Chem. News, lxxi., 292) the acid *may* become so strong that "the complete oxidation of Cr_2O_3 to CrO_3 is practically impossible."

The permanganate may be added in too great an excess. This is an item of general knowledge. Experiments have been described in which 20 per cent of the whole bichromate goes down with the manganese oxides on this account. On the other hand, one may use too little, and fail to complete the oxidation. The addition of permanganate in such excess as to retain a rose tint after boiling a certain number of minutes cannot be accepted as a universal rule, because the production of the rose tint may be so far delayed, by the presence of other elements, that too great a bulk of manganese oxides is accumulated before it can be said to persist at all.

I must explain here that this work on the oxidising effects of permanganate has been done since stating my objections to Mr. Galbraith's process for estimating chromium in ferrochromium, and being thereby led to a justification of our respective positions, I propose to notice Mr. Galbraith's letter in this connection.

The letter (Chemical News, vol. lxxvii., p. 187) is essentially made up of the suggestion that I have misrepresented his paper of 1893 and some very satisfactory test analyses in support of the soda modification.

It has been objected to Galbraith's original process that the sample was not altogether soluble in dilute sulphuric acid. This, along with the low results due to using large excesses of permanganate, are the objections to which I refer as having been examined into in Mr. Galbraith's paper (1893).

The only reason I can offer for having failed to announce prior to 1893 that the large excess of permanganate could be reduced with advantage is that it was a point acted upon in the laboratory where I was trained and was treated as a matter of general knowledge. Moreover, I did not discover it, and even if I had, surely Mr. Galbraith, *who kept his knowledge of the improvement hid away for fifteen years* (1878—93), ought not to chide me for failing to publish a fact which those around me—older and more experienced—regarded as no novelty.

I cannot imagine why, in the fourth paragraph of Mr. Galbraith's letter, he makes a point of his having "tried the effect of the presence of iron" in connection with *some other method*. Mr. Galbraith's clear statement of my objection in paragraph 7 shows him to have understood it to refer only to the soda modification. As I made no criticism whatever of the 1873 process, my objection can in no way be supposed to refer to it.

It is pleasanter to notice that in the latter part of his letter Mr. Galbraith has given the satisfactory tests which he omits from his original (1893) paper, and which, I am happy to say, I can now broadly confirm, as also I can justify my bad results.

I do not presume to blame Mr. Galbraith, and at the same time I claim to be acquitted for having failed to see—or, at least, to state—clearly the precise rôle which the manganous salts play in the operation. The instructions are to dissolve the sample in sulphuric acid (1 : 6) and add permanganate. Mr. Galbraith may add as much permanganate as ever he can get in without causing a permanent rose tint; I add much less, and yet sufficient to completely oxidise the chromic oxide; another operator may add even less than I do. So far, all are right; Mr. Galbraith gives no instructions on this point, although he is admittedly aware (Chemical News, vol. lxxi., p. 316) that the excess mentioned in 1877 has been generally thought too much, and variously reduced. When these varying amounts of permanganate—all sufficient to completely oxidise the Cr_2O_3 to CrO_3—lead, after treatment with soda, to varying recoveries, am I not right in my first contention, viz., that the process needs stating in more definite terms before it can be satisfactorily worked?

Mr Galbraith's letter seems to imply that he believes his accurate results to have been obtained from a soda treated solution containing manganous salts. I can now show that this is not so, except in a small degree, and as there exists no statement on the matter to which I can refer, I beg to submit the following explanations:—

To begin with, the equation on p. 132 should be replaced by—

$$10FeSO_4+8H_2SO_4+2KMnO_4= \\ =5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O.$$

Considering now the behaviour of the manganous sulphate only, we know that when permanganate is added to a neutral solution of a manganous salt they are mutually decomposed. This is the principle of the Volhard and Guyard methods of estimating manganese, and the emphasis laid on the neutral or nearly neutral state of the manganous solution is perhaps accountable for one's overlooking the possibility of such a reaction taking place in the strongly acid solution used in dealing with chrome irons. Such a reaction, however, is possible, and is explanatory of the larger precipitate which in such cases precedes the rose tint.*

Is it possible now to *completely* precipitate the manganous salt formed in the ferro-chrome or steel solution by adding permanganate? If it can be done—and Mr. Galbraith, however unconsciously, has habitually pushed his oxidation to that point—then we have the explanation of the success of the method in his hands.

Let the matter be tested experimentally by adding permanganate to the formation of a faint precipitate of the manganese oxide, and then adding varying amounts of permanganate in excess. If the increasing amounts of permanganate more and more completely precipitate the manganous sulphate, the manganous hydrate to be precipitated becomes less and less, and hence the reducing action complained of less evident. Two grms. of iron were taken in each case, along with 50 c.c. K_2CrO_4 (1 c.c. =0·01 grm. Fe). The solutions were boiled for fifteen minutes after adding the final permanganate, and fractional filtration was employed. Strength of permanganate, 25 grms. per litre. A decided excess of soda was used in each case.

Permanganate to faint precipitate. C.c.	Excess of permanganate. C.c.	C.c. K_2CrO_4 recovered.	Percentage recovery.
28	7	23·12	46·2
28	17	38·6	77·2
28	27	48·2	96·4
28	29	49·5	99·0
28	29	49·9	99·8
28	31*	49·95	99·9

In the last test, marked with an asterisk, the permanganate was not completely decomposed; the result is obtained by treating the filtered fraction with HCl according to Stead's method.

This table supports Mr. Galbraith's results. At the same time it confirms everything I have said, and, pointing out as it does so serious a source of possible error, will, I hope, be received as a friendly contribution. I have only to remark that the continued boiling with the amounts of acid used above (30 c.c. dilute, 1 to 4, H_2SO_4 for 2 grms. Fe) did not worsen the results as would have been evident if the manganese oxides were soluble (as Mr. Leffler finds them to be) in larger amounts of acid.

Mr. Galbraith raises an interesting point in connection with those assays which are allowed to stand for a long time. It does not appear how the manganous salts could be responsible for the error in cases where they had been completely oxidised by the permanganate. May I ask for some further assurance that the error is not due to the causes just pointed out? The manganous sulphate and permanganate reaction in an acid solution is completed only after considerable boiling, and it is quite possible to obtain the rose tint, and then fall short of the complete oxidation of the manganous salt.

Returning to the general behaviour of permanganate, I may say that Stead's modification (*Journ. Iron and Steel Inst.*, 1893, vol. i.) of the acid permanganate process is less subject to incidental errors than any other modification of the process I know. It consists in decomposing the permanganate and manganous oxide by dilute HCl. This not only avoids the error, according to design, of a large precipitate, but by the oxidising effect of the liberated chlorine it also minimises the misfortune of having added too small an excess of permanganate.*

We say that the large excess of permanganate carries down some of the chromic acid—which, to be sure, like many another such an expression, is not a very satisfactory way of accounting for the deficiency, however well it may prepare us to expect it. This carried-down chromate would seem to be more than in contact with the manganous oxides, since we can neither remove it by washing (in reason), nor account for it by filtering fractionally. We are told that the washings from these large precipitates are never absolutely colourless, and that the bond, whatever it is, can be loosened by treating the mixture with soda hydrate. Such characteristics have all along presented themselves in connection with the basic chromates whose interference with separatory methods we have been considering. Does not the coincidence suggest that we may have here another such interference?

Totley, near Sheffield.

* A little manganous sulphate added to a solution overdosed with permanganate readily decolourises it. This seems to be a better way than using more H_2SO_4, as recommended by Galbraith; it may sometimes usefully replace alcohol in that office.

THE SPECTRAL ANALYSIS OF NON-CONDUCTING COMPOUNDS BY MEANS OF THEIR MELTED SALTS.

By A. DE GRAMONT.

THE natural silicates, reduced to a fine powder and dissolved in a pearl of a melted alkaline carbonate, through which the disruptive discharge of a condenser charged by an induction coil strikes, have given me in the spectroscope all the principal lines of silicon (*Comptes Rendus*, Jan. 25, 1897). The greater number of the elements composing or accompanying the silicates also show their presence in a similar manner. I have thus been led to search, in this operation, for a method, generally applicable to non-conducting minerals, which cannot be directly analysed by means of their spectra in the manner already described (*Comptes Rendus*, July 8, 1895).

The continuous and very bright appearance of the line spectra of the components of the minerals studied bring these latter under the conditions of the examination of melted salts, of which I have but recently published the dissociation spectra. Not only the silicates, but the sulphates, sulphides, fluorides, carbonates, oxides, and—apart from minerals—the insoluble non-conducting precipitates, obtained successively in analytical operations by the wet way, all give satisfactory results by this method of investigation. As in the case of all spectral reactions, the sensitiveness differs notably between one simple body and another; it is, however, better as a rule than that of the blowpipe or the wet method.

This method only requires a very small quantity of material, which must be finely ground in an agate mortar, and intimately mixed with the salt destined to disintegrate

* It should be noted that, owing to the presence of large amounts of manganous salts, the ferricyanide test may be falsified by the production of a reddish brown precipitate. This precipitate acts, as may be seen by viewing a blue solution against a reddish paper, not merely by clouding the test drop, but by neutralising the colour also (CHEM. NEWS, lxxvii., 133).

and dissolve it. A small quantity of this mixture is melted in a flame, on the flattened end of a stout platinum wire forming the lower side of the <-shaped arrangement I have previously described, where the apex of the angle is the point where the spark strikes when the two poles are brought close to each other; these poles are connected to the poles of the Leyden jar and the coil.

The melted salt used as the igneous solvent of the mineral has generally been carbonate of lithium, on account of the simplicity of its spectrum, its easy fusibility, and the rapidity of its solvent action on the silicates. Carbonate of sodium gives good results, but it is less fusible, and the maximum of intensity of the spectrum obtained by its use is considerably slower in showing itself than with Li_2CO_3. The two salts have been used concurrently in most of the experiments, and the superiority of the dissolving power of the lithium salt, at a relatively low temperature, appeared to me to warrant its use in all cases of the analysis of a silicate by igneous disintegration.

The small number of the carbon lines, of which I have already described both the position and the appearance in the carbonates (*Comptes Rendus*, July 29, 1897), is in practice reduced to two—657·8 in the red and 426·7 in the indigo. The spectrum of the solvent thus shows very few lines, and, instead of interfering with the observations, they serve as additional data for locating the position of those sought for.

This method offers another advantage, viz., the absence of the air spectrum, which only appears after the volatilisation of the melted salt, or when the flame does not properly envelope it.

The use of other salts has been tried. Boric acid and the borates appeared to be very bad conductors, whether melted or in the state of vapour; the spark passes with difficulty, giving both the spectrum of platinum and of air. Further, the lines of boron can only be obtained under special conditions, above all with regard to the strength of the spark used. There is, therefore, no advantage to be gained by using salts of boron as a solvent, nor is it easy to detect boron by its spectrum of dissociation; it is better, on the contrary, to depend on the well-known green bands it gives in the flame.

We can, on the other hand, make use of the alkaline bisulphates, either for detecting the metals (but we must not go beyond a slight condensation, insufficient to cause the appearance of the sulphur lines), or for studying the most refrangible part of the spectrum, where no sulphur lines are to be found.

The source of heat to be used varies with the salt; for Li_2CO_3 an ordinary spirit lamp will suffice, but with the other carbonates or with the bisulphates it is necessary to use a Bunsen burner or a petroleum eolipyle.

The general arrangement of the apparatus, and the method of making the observations, is the same as that which I adopted when studying the spectra of melted salts. The condensation only is varied; it has been reduced to one jar, in the case of the metals only, without causing the lines of the metalloids to appear. If we have any fear of the formation of reducible metallic compounds which might attack platinum, the lower platinum spatula may be replaced by a morsel of pure Siberian graphite, hollowed out like a small crucible, to contain the drop of melted mixture, and held in the flame by a pair of platinum-tipped forceps.—*Comptes Rendus*, vol. cxxvi., No. 16, 1898.

ON THE SPECTRUM AND THE NATURE OF NEODYMIUM.

By EUG. DEMARCAY.

Since the important work done by M. Auer von Welsbach (*Monats. f. Chem.*, 1885, p. 477), it has been announced that the number of lines in the spectra of neodymium and praseodymium vary considerably, and that these variations prove the existence of several distinct simple bodies (according to some authorities, there are as many elements as there are absorption-bands). But the proof of these variations has never yet been shown, nor has any work been published with the object of establishing the truth or the falsity of the statement. I decided to submit a considerable quantity of didymium, freed from lanthanum and cerium, to a series of fractionations by the method of ammoniacal nitrates (Auer). They gave me a double nitrate which, when melted in its own water of crystallisation and observed through a thickness of more than 0·1 metre, no longer showed any trace of the principal band of praseodymium. This nitrate was the starting-point for a fresh lot of fractionations which enabled me to eliminate, on the one hand, samarium and the neighbouring earths in notable quantities, and, on the other hand, a slight trace of praseodymium. I thus obtained more than twenty successive portions which exhibited the most striking identity from every point of view. The praseodymium was invisible through thicknesses of more than 0·1 metre of the melted nitrate; the samarium could not be detected either by its absorption bands near H, usually so intense, or by its strong ultra-violet rays in the spark spectrum, or in its fluorescent spectrum in sulphate of calcium.

To convince myself that, in spite of the identity of the spark spectra of the first and last portions, there was no earth present not having an absorption spectrum or a discernible spark spectrum, I had recourse to a spectro-colorimeter. The result was negative; both portions showed the same absorption-spectra with the same intensity; it was impossible to detect the slightest difference between any of the bands. In my opinion, therefore, we must conclude that, contrary to the statements of several *savants*, neodymium is a simple body, and not a mixture of elements. Several very much shorter series of fractionations enabled me, in fact, to observe the spectra of samarium and of praseodymium individually rapidly increasing and diminishing. I may add that neodymium from entirely different sources (cerite, samarskite, mosandrite) has always given me, when properly purified, identically the same spectrum. The opinion that neodymium is composed of earths incomparably more difficult to separate than no matter which other group of elements among the rare earths, is thus shown to be devoid of experimental foundation. Other methods of fractionation have led me to the same results, though in a much slower manner.

Oxide of neodymium, prepared from the oxalate by prolonged calcination in the air, is not grey, greenish, or rose coloured, as various authors have stated, but of a clear bright blue colour, with lilac reflections in the mass. Very small traces of praseodymium, samarium, or terbium affect the colour to a marked degree; this is therefore a very good indication of its purity. The colour of the salts of neodymium is of a lilac-blue through only a slight thickness; through a medium thickness, it is a rose-violet; in concentrated solutions, through a thick layer, it is of a very rich reddish violet colour. Even small proportions of samarium or of praseodymium suffice to change the colour to a more or less yellow or brownish red, such as has always been described as the colour of neodymium up to the present time.

In the form of chloride (a 10 per cent solution of the oxide in HCl, through a thickness of 0·036 metre) neodymium gives the following bands:—

732·4	
691·0	
680·4	Strong.
673·1	Faint.
637·3	
629·2	Very faint double.
623·4	
578·3	About the middle of the very strong band.
532	About the middle of the strong band.

522	Fairly strong.
510·9	Very strong in the middle.
476·8	Strong.
469·1	,,
462·4	Cloudy, diffuse, fairly strong.
435·1	Faint.
429·4	Very faint.
428·1	Strong.
420 (about)	Very faint.

The whole of the first portion of this spectrum, up to 510·9 inclusive, is identical with that described by M. Auer von Welsbach (*loc. cit.*). But this *savant*, out of all the following lines, only mentions 428·1. I cannot easily understand the omission of the lines 476·8 and 469·1 (very near to a praseodymium band, but certainly not due to it), and 462·4, which are all strong, and can be easily seen even in a fairly weak solution. The presence of a certain amount of samarium, as shown by M. Lecoq de Boisbaudran, causes the blue bands I have just mentioned to disappear in a vague and hardly visible nebulosity. Is this perhaps the reason of their omission by M. Auer and, more recently, by M. Brauner (*Chem. Soc. Trans.*, 1898)?

The spectrum varies enormously in certain bands with the nature of the acid present. For example, the small group towards 630 is unrecognisable in nitric solution. M. de Boisbaudran has already noticed several analogous facts.

I will finish by expressing the hope that chemists making observations of absorption-spectra will, in future, describe accurately the exact composition of the solution and the thickness of the layer through which it has been examined: without these data, we cannot well interpret the results published in many papers.—*Comptes Rendus*, cxxvi., No. 14.

ON THE YTTRIC EARTHS CONTAINED IN THE MONAZITE SANDS.*

By P. SCHÜTZENBERGER and O. BOUDOUARD.

THE pure yttric oxides, after being converted into nitrates, are submitted to partial decomposition at a temperature of from 315° to 325°. The operation is carried on in a cylindrical platinum crucible plunged by any convenient means into a bath of nitrates of potassium and sodium in equal parts. The melted nitrate commences by giving off nitrous vapours, it then gets pasty, and finishes by forming a crystalline mass, solidifying at 315°. When all decomposition appears to have finished, it is allowed to cool, and is then treated with boiling water. The mass divides into an insoluble sub-nitrate and a soluble part consisting of a neutral nitrate; this latter, evaporated to dryness, is submitted to the same treatment, and gives a fresh insoluble sub-nitrate and a soluble neutral nitrate. The sub-nitrates thus obtained are washed with warm water and transformed into sulphates, and the atomic weight of each one is determined by a prolonged calcination of these sulphates at a bright red heat.

It is a very easy matter to establish a theory for this decomposition of the yttric nitrates at the temperature of 325°; it should be effected according to the following reactions:—

$$2[(NO_3)_6M_2] = (NO_3)_6M_2,M_2O_3 + 3N_2O_5,$$

$$(NO_3)_6M_2,M_2O_3 = (NO_3)_6M_2 + M_2O_3 \text{ aq.}$$

Adding these two equations member to member we get—

$$2[(NO_3)_6M_2] = (NO_3)_6M_2 + 3N_2O_5 + M_2O_3 \text{ aq.}$$

Each partial decomposition would thus separate the half of the oxide entering into the reaction. In the numerous experiments which were made, the weight of the oxides obtained often represented one-third of the oxide used, and several times a half. This variation certainly points to this, that the formation of crystalline crusts during the decomposition prevents this latter from being complete. But if we allow the decomposition to proceed for a sufficient length of time, we always obtain the half of the oxide which has entered into the reaction.

Results Obtained.—We shall now give some of the series of fractionations which have appeared to us to be of the greatest interest. The two methods—that of fractional crystallisation and that of fractional fusions—have, further, been combined.

A.—Two sub-nitrates were made, and each separate portion has been submitted to a fractional crystallisation.

Sub-nitrate No 1.

This sub-nitrate, after having been transformed into nitrate by simple solution in nitric acid, was itself partially decomposed into two other subnitrates.

SUB-NITRATE No. 1 (1).

First Crystallisation.

Atomic weight	123·2
Anhydrous sulphate used ..	3·6140
Oxide obtained	1·9910

Second Crystallisation.

Atomic weight	122·25
Anhydrous sulphate used ..	2·8145
Oxide obtained	1·5460

SUB-NITRATE No. 1 (2).

First Crystallisation.

Atomic weight	114·7
Anhydrous sulphate used ..	3·7790
Oxide obtained	2·0260

Second Crystallisation.

Atomic weight	100·85
Anhydrous sulphate used ..	4·7238
Oxide obtained	2·4138

Sub-nitrate No. 2.

First Crystallisation.

Atomic weight	102·4
Anhydrous sulphate used ..	2·7330
Oxide obtained	1·4020

Second Crystallisation.

Atomic weight	100·1
Anhydrous sulphate used ..	2·5250
Oxide obtained	1·2840

Mother-liquors from Sub-nitrate No. 2.

First Crystallisation.

Atomic weight	100·9
Anhydrous sulphate used ..	4·7230
Oxide obtained	2·4095

Second Crystallisation.

Atomic weight	96·0
Anhydrous sulphate used ..	2·5625
Oxide obtained	1·2815

Third Crystallisation.

Atomic weight	94·0
Anhydrous sulphate used ..	2·3482
Oxide obtained	1·1645

The sulphate (at. wt. = 96) was submitted to a fractional crystallisation:—

First Crystallisation.

Atomic weight	98·1
Anhydrous sulphate used ..	3·4410
Oxide obtained	1·7350

Second Crystallisation.

Atomic weight	93·0
Anhydrous sulphate used ..	2·1925
Oxide obtained	1·0825

* *Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 6.

The sulphate (at. wt. = 98·1), after having been calcined, was again transformed into nitrate and sulphate. Two more crystallisations were made:—

First Crystallisation.

Atomic weight	99·65
Anhydrous sulphate used	3·2980
Oxide obtained	1·6740

Second Crystallisation.

Atomic weight	94·5
Anhydrous sulphate used	2·1037
Oxide obtained	1·0473

The first crystallisations of these two fractionations (at. wts. = 98·1 and 99·65) were united and submitted to a fresh fractional crystallisation:—

First Crystallisation.

Atomic weight	101·1
Anhydrous sulphate used	5·5187
Oxide obtained	2·8172

Second Crystallisation.

Atomic weight	96·7
Anhydrous sulphate used	3·7020
Oxide obtained	1·8565

The sulphate (at. wt. = 101·1) was again separated by two fractionations:—

First Crystallisation.

Atomic weight	102·35
Anhydrous sulphate used	4·5607
Oxide obtained	2·4320

Second Crystallisation.

Atomic weight	98·0
Anhydrous sulphate used	4·3135
Oxide obtained	2·1750

The oxide which gave on analysis 102·35 was added to the oxide resulting from the calcination of the corresponding sulphate, and was transformed into nitrate and sulphate by making use of quite a fresh method of procedure. Before evaporating to dryness, the acid mother-liquor which remained over the crystals was decanted; the crystals were then gently calcined and, after dehydration, dissolved in water. This was crystallised and separated into two portions:—

First Crystallisation.

Atomic weight	104·1
Anhydrous sulphate used	3·5995
Oxide obtained	1·8590

Second Crystallisation.

Atomic weight	99·5
Anhydrous sulphate used	2·7840
Oxide obtained	1·4125

Acid Mother-liquors.

Atomic weight	102·6
Anhydrous sulphate used	2·4702
Oxide obtained	1·2682

The sulphate (at. wt. = 104·1) was separated into two fresh portions, which gave:—

First Crystallisation.

Atomic weight	104·55
Anhydrous sulphate used	2·1993
Oxide obtained	1·1375

Second Crystallisation.

Atomic weight	97·5
Anhydrous sulphate used	1·4055
Oxide obtained	0·7070

As is shown by the first results we have obtained at different times atomic weights represented by figures very close to 98. We have re-united all the oxides responding to this condition, and have made a fresh fractional crystallisation:—

First Crystallisation.

Atomic weight	97·1
Anhydrous sulphate used	2·3237
Oxide obtained	1·1675

Second Crystallisation.

Atomic weight	97·45
Anhydrous sulphate used	2·2422
Oxide obtained	1·1280

Third Crystallisation.

Atomic weight	97·7
Anhydrous sulphate used	3·1568
Oxide obtained	1·5900

Fourth Crystallisation.

Atomic weight	94·5
Anhydrous sulphate used	1·3310
Oxide obtained	0·6615

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF ZIRCONIUM.*

By F. P. VENABLE.

I. *Purification of the Material.*

Preparatory to entering upon the revision of the atomic weight of zirconium, a study was first made of the best method of decomposing zircons and securing pure preparations (*J. Anal. Appl. Chem.*, v., 551—554). The pulverised zircons were fused in nickel crucibles with sodium hydroxide and sodium fluoride. The melt was washed, dissolved in hydrochloric acid, and filtered from some of the silica and from undecomposed zircon. This filtrate was evaporated to dryness to render the silica insoluble, again dissolved in diluted hydrochloric acid, and filtered, and this was repeated two or three times. The further purification consisted in precipitation by ammonium hydroxide, washing, and re-solution in hydrochloric acid, followed by repeated crystallisations from boiling concentrated hydrochloric acid. After it had been thus purified it was found that traces of silica were still present. To remove these the chloride was dried, ignited, and the powdered zirconia was again and again treated with hydrofluoric acid. After driving this off, the zirconia was again melted with potassium hydroxide (purified by alcohol), taken up with hydrochloric acid, and subjected once more to crystallisation from strong hydrochloric acid. These crystallisations varied in number from twenty to thirty odd, and, if those which preceded the second fusion are to be taken into account, exceeded sixty in all. Just before using in the series of determinations of the atomic weight, this purified chloride was filtered by means of an unglazed porcelain suction-filter which had been cleaned by boiling for several days in strong hydrochloric acid, and then standing three days in fresh cold hydrochloric acid. The last acid was entirely free from colour. This filter was kept under distilled water when not in use. The filtration had to be carried out with hot solutions, but the liquid was not in contact with the filter more than five or six minutes.

When this work was undertaken it was believed that the substance under examination was zirconium tetrachloride. This belief was based on the work of Linnemann and upon my own determinations of the zirconia, these agreeing fairly well with the amount required for $ZrCl_4$. At the close of the determinations of zirconia recorded later, some determinations of the chlorine present were made, and were found not to agree at all with the amount requisite for the supposed formula. The matter did not seem easy of explanation, and the work was laid aside until time could be gotten for a more thorough study of

* From the *Journal of the American Chemical Society*, xx., No. 2.

this body. My study of the oxychlorides of zirconium has shown that there at least three :—

$ZrOCl_2 \cdot 3H_2O$ when crystallised from strong hydrochloric acid.

$ZrOCl_2 \cdot 8H_2O$ when crystallised from water.

$ZrOCl_2\ 6H_2O$ when precipitated by hydrochloric acid from an aqueous solution.

All of these, dried in a stream of hydrogen chloride at 100° to 125°, have the formula $ZrOCl_2 \cdot 3H_2O$, and this water is lost only by heating from 180° to 210°.

The liquid filtered as above is clear and bright, and soon begins to deposit groups of needle-like crystals, or it crystallises to a solid mass if a large amount of the salt is present. In several cases the crystallisation was repeated two or three times from acid after this filtration, but no perceptible difference was made in the results. These crystals take up a considerable amount of acid which cannot be drained off. In this acid they easily melt, and if the excess is removed under a stream of hydrochloric acid gas the chloride can be gotten in the form of a dry white powder. The oxychloride can be thus dried without decomposition under a stream of hydrochloric acid gas at the temperature of 100° to 125° C. to $ZrOCl_2 \cdot 3H_2O$. As the difficulty in drying this salt was the main stumbling-block in the way of previous workers, interfering with its use for atomic-weight work, the removal of this obstacle seemed to place it among the most suitable of the compounds to be used for the purpose. A full account of the examination of the chlorides will be published shortly. Other compounds have been examined also in the progress of this work, and, though they may be used hereafter, they have seemed to me to present more difficulties than the chloride, and so this has been taken first.

Previous Determinations of the Atomic Weight.

It is perhaps best to give here a brief outline of previous determinations of the atomic weight of zirconium. Six such series have come under my notice. In three of these the sulphate was used, and in the others the chloride and the double fluoride of zirconium and potassium were used, and in one the selenate.

The determinations of Hermann (*J. Prakt. Chem.*, xxxi., 77), by means of the chloride, can be dismissed as untrustworthy, because of his failure to overcome the difficulties inherent in the use of the chloride as shown by Bailey's work and my own.

The work of Marignac upon the double fluoride I am not in a position to criticise properly, except in so far as to say that his analyses are not very numerous, and that they show a range of nearly three units in the atomic weight.

In 1825 Berzelius ignited the sulphate and gave six determinations of the ratio of the sulphate to the oxide. In some of the experiments he also precipitated the zirconium hydroxide by means of ammonium hydroxide, and determined the sulphuric acid in the filtrate by precipitation with barium chloride.

Mats Weibull also used the sulphate, and reports seven experiments with an entire consumption of 8·2335 grms. Bailey's own determinations number eight, using in all more than 16 grms. He gives full data as to his work, and it is well done and merits very careful attention. The following table is copied from his article (CHEM. NEWS, lx., 17). The figures have been re-calculated to the basis of O=16.

	Mean.	Maximum.	Minimum.	
Zr : Cl	88·77	—	—	Hermann
ZrO_2 : HCl ..	90·14	90·98	89·29	Hermann
$K_2ZrF_6 : K_2SO_4$	90·53	92·80	90·06	Marignac
$ZrO_2 : K_2SO_4$..	90·64	91·26	90·24	Marignac
$K_2ZrF_6 : ZrO_2$.	90·8	91·3	89·9	Marignac
$Zr(SO_4)_2 : ZrO_2$	89·45	92·65	89·27	Berzelius
$Zr(SO_4)_2 : ZrO_2$	89·48	90·38	89·13	Mats Weibull
$Zr(SO_4)_2 : ZrO_2$	90·65	90·78	90·46	Bailey

It is manifest that the determinations based upon the ignition of the sulphate are the only ones worthy of further attention. A brief criticism of these is necessary. First, as to Mats Weibull, Bailey says that the temperature used by him in freeing the sulphate from the excess of sulphuric acid was some 50° too low. This would of course give him variable and low results. Berzelius does not give exact data as to temperature used, but he seems to have heated the sulphate too high in driving off the excess of acid. Possibly more stress is to be laid upon the question of the purity of his sulphate and the correctness of the assumption that he had in hand the normal sulphate.

Bailey concludes from his experiments that the sulphate is stable up to 400° C., and that the excess of sulphuric acid can be completely driven off by the use of a temperature between this and 350° C. He further states that a mixture of the salt and free acid, as prepared by him, when heated to this temperature until constant, yields the normal sulphate. It must be said that he gives no proofs of this beyond the amount of zirconia found in his atomic weight determinations.

Whilst certain criticisms of the work of Bailey have occurred to me, I will refrain from mentioning them until I have had opportunity to repeat his experiments, and so make myself more familiar with the details of his method.

One criticism I can venture upon now, however. I doubt whether it is possible to ignite, without loss, zirconia along with ammonium carbonate, as was done by Berzelius and by Bailey to remove the "last two or three m.grms. of sulphuric acid." I have not ventured to use this method in getting rid of the chlorine which is held just as tenaciously as the sulphuric acid, as I feel sure that it could not be done without loss. Bailey adopted extraordinary precautions to prevent this loss, but it seems to me that it is not the currents of the external atmosphere, as he maintains, which are to be most avoided, but the mass of escaping vapour of the ammonium salts. It is easily possible for him to have lost several m.grms. of the finely-divided zirconia in his way, and, as he states, each m.grm. was equivalent to a variation of 0·25 in the atomic weight.

The Weighings.

In the following experiments the amounts of substance used varied from 1 to 5 grms. To avoid the disadvantage of a small error causing a large variation in the result, I would gladly have used larger amounts of the chloride, but many difficulties met me there. The purification of the zirconium chloride is slow and costly. It is best carried out in small portions of a few grms. at a time. Some 50 grms. have constituted the stock at my command. The drying of large portions and the subsequent ignition would be exceedingly tedious and time-consuming, besides requiring such apparatus as could not be well afforded. Five or six grms. have been about the largest amounts that could be well handled at one time. Even such an amount as that required from sixteen to twenty days for the completion of the experiment. It could not be safely hurried through in shorter time.

The weighings were carried out upon an excellently constructed Sartorius balance, intended for a load of 200 grms. The heaviest apparatus used weighed less than 60 grms. The weights were corrected by one which had been compared with the standard at Washington. All objects were weighed against a tare of as nearly the same size, form, and weight as possible, all of the flasks, crucibles, &c., being made in pairs. This partly avoided the necessity for a reduction of the weighings to a vacuum and corrections for moisture, pressure, &c. Such corrections would have had little meaning in comparison with the other inaccuracies of the process and manipulation, and could only serve to give a false appearance of excessive accuracy. The objects were left one half-hour in the balance-case before weighing, experiments having

shown that this time was sufficient. Of course the adjustment of the balance was carefully watched, and the balance, which has been used very little, was put to no other use during the progress of these experiments.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

A Conversazione was held at the Royal Society's Rooms at Burlington House on Wednesday last, the 11th of May, the guests and Fellows being received by Lord Lister and the Members of the Council.

Among the numerous exhibits we noted Professor Hele Shaw's Experiments on the Flow of Water, in which it is shown that stream-lines obtained in layers of inappreciable thickness have been found to be identical in practice with those arrived at mathematically.

Mr. Campbell Swinton showed some new forms of Crookes Tubes, the one of most interest being a fresh pattern of the experiment proving the physical movement of the molecules in a highly exhausted tube.

Dr. Armstrong had some attractive coloured photographs of those fascinating phenomena in the Yellowstone Park, U.S.A.

Close by were some excellent specimens of "Naturographs," produced by Dr. Selle's process of photography in natural colours. Three specially prepared negatives are taken through red, blue, and green glass screens respectively. From the negatives three collodion positives are produced, which, after development in complementary colour baths, are superimposed, the result giving the complete picture. The time of exposure is from 3 to 30 seconds.

Prof. Roberts-Austen exhibited an Apparatus to Illustrate M. Daniel Berthelot's Interference Method of Measuring High Temperatures. One of the beams of light in an interference apparatus traverses a heated porcelain tube, and the other beam traverses a tube of equal length containing rarefied air. When interference takes place it indicates that the air in the two tubes is equally rarefied, and therefore the temperature of the heated tube can be calculated from the pressure of the air in the other tube.

But perhaps the most interesting and important of all the exhibits was Prof. Oliver Lodge's demonstration of Recording Telegraphic Signals through Space by means of the Hertz Wave, the receiving apparatus being a Muirhead syphon recorder.

He also shows some Apparatus illustrating the Improvements in Magnetic Space Telegraphy. The discharge of a condenser or Leyden jar round a large wire coil sets up an alternating magnetic field, which excites induced currents in another distant condenser-circuit tuned to the same frequency, causing the second Leyden jar either to overflow into a coherer or to disturb a Rutherford detector or a telephone so as to give a signal. The detector shown is a special series of small free coils and granular microphones, each coil in a permanent magnetic field, and so connected to the microphone of the next that a very feeble alternating current in the first of the series is able to make a telephone in the last emit a loud sound, or through a Langdon-Davies relay, to ring an electric bell and work a Morse sounder. A tone-telephone is also shown, which acts as a highly syntonised "call."

The Hon. C. A. Parsons had some photographs and models of his High Speed Engine, as used on the *Turbinia*. A small model of his propeller was working at about 1000 revolutions per minute.

A curious lot of crabs were shown by the Marine Biological Association. They were taken principally from the neighbourhood of Plymouth, and illustrate the remarkable faculty of self-protective concealment.

Sir David Salomans exhibited his Pseudoscope for obtaining stereoscopic effects by means of a single picture.

At 10.45 an interesting discourse was given by Sir Norman Lockyer on the Recent Solar Eclipse, as observed at Viziadrug. It was illustrated by excellent photographs.

ROYAL INSTITUTION.

General Monthly Meeting, May 9th, 1898.

Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members:—Messrs. Hugh Bell, H. M. Brunel, B. Knight, L. Phillips, and A. M. Smale.

The following Vice-Presidents for the ensuing year were announced:—Sir William Crookes, Sir Edward Frankland, Sir William Huggins, Dr. Ludwig Mond, the Hon. Sir James Stirling, Sir H. Thompson, Sir James Crichton-Browne (Treasurer), and Sir Frederick Bramwell (Hon. Secretary).

The Right Hon. Lord Rayleigh was re-elected Professor of Natural Philosophy in the Royal Institution.

NOTICES OF BOOKS

The Workmen's Compensation Act, 1897 (60 and 61 Vict., cap. 37). With Copious Notes. By W. Addington Willis, LL.B. (Lond.). Third Edition. London: Butterworth and Co.; and Shaw and Sons. 1898. Pp. 96.

The necessity for such a book as this is clearly shown by the rapidity with which the editions are following each other. There is not much comment to be made on this latest edition beyond the fact that it has been thoroughly revised, and some further notes added to the section relating to Schemes which may be submitted to the approval of the Chief Registrar of Friendly Societies, to be substituted for the provisions of the Acts. It is a very serious matter for the large employers of labour, and we hope the Frankenstein which successive Governments have been building up and fostering for the last fifty years will not turn out to be too strong for them to exorcise. There have been hopeful signs of improvement recently, but it is a thankless task to be a "master."

Mr. Willis's book is eminently practical, and it is easy to see that it is appreciated.

General Elementary Science. Edited by Wm. Briggs, M.A., F.C.S., F.R.A.S. London: W. B. Clive, University Correspondence College Press. Pp. 140.

Now that the University of London has made General Elementary Science a compulsory subject for the Matriculation examination, and so long as we must have examinations, a book such as the one before us—which has been compiled with a special view to this particular one—cannot fail to be of use to the unhappy examinee.

A noteworthy feature of this volume is that, comprising as it does several subjects, it is not all written by one man. Section I., on Mechanics, has been prepared by Prof. Bryan, D.Sc., F.R.S., and A. G. Cracknell, M.A.; Section II., on Heat, Light, and Electricity, by John Don, M.A., B.Sc.; and Section III., on Chemistry, by G. H. Bailey, D.Sc. Ph.D., and Frank Beddow, D.Sc., Ph.D.

The volume being, as has been shown, divided into three Sections, each Section is subdivided into a number of short numbered paragraphs, each with a special heading, and dealing simply with the subject of that heading.

After a certain number of paragraphs we find a set of questions and problems, the answers of which are to be found at the end of each Section.

The whole arrangement appears to us to be satisfactory, and likely to be of considerable service to students preparing for the examination in question. The book is well got up, and contains numerous illustrations.

The Gas Engineer's Pocket Book. By H. O'Connor, A.M.I.C.E. London: Crosby Lockwood and Son. 1898. Pp. 438.

"The Gas Engineer's Pocket Book" comprises tables, notes, and memoranda relating to the manufacture, distribution, and use of coal gas, and the construction of gas works, &c. It is founded principally on copious notes taken and prepared by the author, during his daily work for many years past: they were at first intended for personal use only; fortunately, however, for gas engineers in general, he has arranged them in their present form and offered them to the world as a pocket book of reference.

This volume differs from many similar pocket books, in that it is of larger size than most of them, and not only contains the same old familiar sets of tables, but also a large amount of letterpress, describing, in well-chosen language, the different processes used in connection with gas-making, &c. It is well printed and bound, and will make a useful addition to the book-shelf.

First Year's Course of Experimental Work in Chemistry. By E. H. Cook, D.Sc. (Lond.), F.I.C. London and New York: Edward Arnold.

We cordially agree with the first sentence in the author's preface, viz., "To be successful in passing an examination is one thing, perhaps a good thing, but to have a sound knowledge of the subject is another and far more important matter." Students not only of chemistry, but of all other subjects, cannot do better than get this maxim firmly fixed in their minds. Examinations are a crude but popular method of sorting students, and too often the one who can "cram" well takes undue honours from the real plodding students who retain what they may take a longer time in learning.

Mr. Cook's book is well adapted to giving the student a good grounding in physical as well as chemical science, —in fact, it is as much a book of manipulations as of chemical facts and theories, and in the final chapter the principal laws which govern the experiments described in the preceding ones are carefully summarised. The book is likely to be of great use to beginners.

An Elementary Course of Practical Organic Chemistry. By F. C. Garrett, M.Sc. (Vict. et Dunelm), and A. Harden, M.Sc. (Vict.), Ph.D. London, New York, and Bombay: Longmans, Green, and Co. Pp. 72. 1897.

The small volume we have just looked through can only be considered as giving the merest outline of organic chemistry; in fact, the authors state that care has been taken to describe only such experiments as can be successfully carried out in the somewhat limited periods of time which are at the disposal of students in technical schools and colleges. If the student who goes through this primer will remember that he has still a great deal to learn, all may be well with him, and the instruction herein gained will make a good foundation for more serious work to follow.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 14, April 4, 1898.

Electric Conductivity of Solutions of Permanganate of Potash.—Emmanuel Legrand.—The author used Kohlrausch's method, with a telephone and an alternating current. The experiments made were on solutions containing 1/16, 1/32, 1/64, 1/128, 1/256, and 1/1024 of a molecule of permanganate of potash per litre; the values of the molecular conductivities observed varied from—

		Conductivity.	
		Observed.	Molecular.
1/16 normal	25° C.	0·00716	0·1145 10^2
	35	0·00869	0·1390
	45	0·00992	0·1587
	to		
1/1024 normal	25	0·00012	0·1228
	35	0·00015	0·1536
	45	0·00015	0·1536

The table (a part only of which is here given) shows that at the same temperature the molecular conductivity increases with the dilution, and that when the temperature is high the conductivity increases the less rapidly as the temperature is increased.

Comparison of the Values of the Atomic Weights of Hydrogen, Nitrogen, and Carbon deduced from Physical Data with the Values deduced from Chemical Analysis.—D. Berthelot.—The molecular volume of a gas at 0° at the atmospheric pressure being equal to 1 for a gas following Mariotte's law exactly, this volume has the value $1 - a$ for a gas which does not follow it. The molecular volume of hydrogen which is less compressible at 0° than the law requires is thus higher than 1; that of the other gases which are more compressible is lower than 1. The atomic weights of the four gases, calculated according to the author's formula, are—H = 1·0074, N = 14·007, C = 12·007, O = 16, with a $\pm$ error of 1/5000th on these figures.

Isoquinolein and Tetrahydroisoquinolein.—Marcel Delépine.—The union of the benzenic nucleus with the pyridic nucleus to form the base C_9H_7N can be effected in two ways and gives rise to two isomers—quinolein and isoquinolein. Isoquinolein is fusible at 23° and boils at 243° without changing. Its molecular heat of combustion is—At constant volume, 1123 cals.; at constant pressure, 1123·7 cals. From which it follows that the heat of formation is $C_9 + H_7 + N = C_9H_7N$ (solid) −35·5 cals. Hydroisoquinolein, $C_9H_{11}N$, is a liquid boiling at 234°, attracting carbonic acid from the air, like benzylamine. Its heat of combustion at constant volume = 1213·75 cals., and at constant pressure = 1215·0 cals.; therefore its heat of formation is $C_9 + H_{11} + N = C_9H_{11}N$ (liquid) +13·2 cals. The chlorhydrates only have been studied. The displacement of isoquinolein in its chlorhydrate by potash gave at 20°8 cals.: if isoquinolein was displaced in the anhydrous state we should get 13·6 − 6·35 = 7·25 cals. This clearly shows that the base is displaced in the form of hydrate. The calculated value would be: 13·6 − 5·41 = 8·2 cals.

Estimation of Small Quantities of Carbonic Oxide in the Air and in Normal Blood.—L. de Saint-Martin. —A reply to a recent paper by M. A. Gautier, who had cast doubts on the extreme accuracy of the present author's method of estimation.

On the Spectrum and the Nature of Neodymium.—Eugene Demarçay.—(See p. 219).

Action of Oxidants on some Nitrified Bodies.—Oechsner de Coninck.—The author gives the results of his experiments on the oxidation of some of the nitrified functions of the amines. Hydroxylamine is instantaneously decomposed, with disengagement of nitrogen, by solutions of hypochlorites of Ca, Na, K in an excess alkali. Acetaldoxime is easily decomposed in excess of the base. The diamines do not give off much nitrogen, but ammonia is separated. Carbonate of *guanidine* is immediately decomposed by the hypochlorites. It makes a good lecture experiment. The solution first takes a deep yellow colour, then an orange-red. The reaction is very distinct with the hydrazines; nitrogen commences to come off at once and continues to do so until cold. Cyanic and cyanuric acids are immediately destroyed by hypochlorites, but the results with most of the alkaloids, such as piperidine, nicotine, cocaine, &c., were negative; with antipyrine, on the contrary, a certain quantity of nitrogen was given off.

A Combination obtained with Nitrate of Mercury and Trimethylcarbinol.—G. Denigès.—In endeavouring to find out whether the tertiary alcohols, which resemble the phenols in so many ways, would furnish compounds with mercury of the same order as the latter, the author finally succeeded in isolating a compound obtained by the action of mercuric nitrate and trimethylcarbinol, but he was unable to prepare corresponding compounds with the other tertiary alcohols. He was, however, more fortunate with mercuric sulphate, which in a strongly acid solution proved to be a much more general reagent, especially with the ethylenic carbides. Mercuro-mercuric-dimethyl-ethylenic nitrate, which was formed, detonates by a shock, or on the temperature being raised to 80°; treated with HCl it effervesces like a carbonate, and gives off dissymmetrical dimethylethylene, leaving a residue, formed of mercuric and mercurous chlorides. The compound is not attacked in the cold by caustic alkalies, but after boiling for a few minutes it gives a brown precipitate, a mixture of mercuric and mercurous oxides. These different reactions show that it contains mercury in two states (at the maximum and the minimum). Its formula is—

$$\left.\begin{matrix} NO_3Hg \\ NO_3Hg_2 \end{matrix}\right\rangle C_4H_8.$$

Berichte der Deutschen Chemischen Gesellschaft.
1898, No. 3.

Gasometric Apparatus.—Otto Bleier.—The author describes an apparatus by which great accuracy in measuring gases can be obtained. A double pipette, in which the gas is measured, is connected with a compensator, through a differential manometer. Readings can be taken accurately to 0·001 per cent.

Action of Hydroxylamines on Imidchlorides and Anilidoximes.—H. Ley.—Hydroxylamine was dissolved in absolute alcohol and decomposed with the calculated amount of sodium ethylate. After rapid washing from common salt, the solution was decomposed with a solution of benzanilidimid chloride in absolute ether and left to stand for some hours. After distillation of the solvent the anilidoxime was extracted with water and re-crystallised from alcohol (m. p. 138°). Benzenyl-*o*-toluidoxime, benzenyl-*p*-chloranilidoxime, and benzenyl-*o*-nitranilidoxime were also prepared, and the action of imidchloride on α and β substituted hydroxylamines was investigated.

The End-product of the Action of Nitrogen Chloride on Dimethylaniline.—W. Hentschel.—The author studies the decomposition products of nitrogen chloride on dimethylaniline in different solutions. An alcoholic sodium solution gives tetrachloraniline (m. p. 88°). By boiling a 20 per cent solution in absolute alcohol for several hours, besides methylamidhydrochloride, he succeeds in isolating the symmetric trichlorphenol. With nascent hydrogen it yields trichlormethylaniline.

Synthesis of Naphthindol Derivatives.—O. Hinsberg and A. Simcoff.—By boiling aromatic primary or secondary amines with glyoxal-sodium bisulphite in aqueous dilute alcoholic solution, either derivatives of glycocoll or indosulphurous acid are obtained. In the latter way react α and β naphthylamines, monoalkylnaphthylamines, and some monoalkylanilines. From the products of such reactions the authors prepare various naphthindol derivatives.

Chemical Nature of Diastase.—Thomas B. Osborne.—The author justifies his own statements made in a former paper, which were contradicted by Wroblewski. His own preparation of diastase was much stronger than Wroblewski's in its inverting power on starch, and when heated to 50° or 60° did coagulate. Also it cannot contain any arabine, because it gives the characteristic test for albumin, and especially the biuret reaction, which would be obscured by the presence of a carbohydrate.

Products of the Action of Formaldehyd on Gallic Acid.—Richard Möhlau and Leopold Kahl.—The authors obtained four products by the action of formaldehyd on gallic acid. Two of these were crystalline, one soluble and the other almost insoluble, and two amorphous, one soluble and one insoluble, methylendigallic acids.

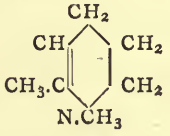
Formaldehydtrioxyfluorondicarboxylic Acid.—R. Möhlau and L. Kahl.—The authors prepare this substance from the slightly soluble crystalline methylendigallic acid. The latter is dissolved in strong H_2SO_4 and warmed gently on the water-bath to about 50°; the solution is first green, then intensely blue. Directly the blue colour appears it is cooled, and the calculated quantity of nitrosylsulphuric acid added. The reaction begins at once, but the mixture must stand for twenty-four hours before it is complete, when the dye can be extracted. It is a violet crystalline powder. Various salts of the acid are also prepared.

Occurrence of Choline and Trigonelline in the Seeds of Strophanthus and the Preparation of Strophanthine.—Hermann Thoms.—The author finds that the two bases choline and trigonelline, are found in the seeds of *Strophanthus*, beside strophanthine.

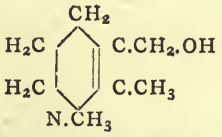
α-Methylpyrroline, N-methyl-α-methylpyrroline, and N-methyl-α-methylpyrrolidine.—R. Heilscher.

Condensation Products of Furfurols and Furfuracroleins.—H. Röhmer.—Furfurol was condensed by the two acids, pyroracemic and phenylacetic acid, and the products examined; also a new series of condensation products of furfuracroleine prepared.

Isomers in the Piperidine Series.—A. Ladenburg.—The author gives to the substance which is obtained by the action of formic aldehyd on—



the formula—



By adding on 2 atoms of H, and subsequent removal of a molecule of H_2O, it forms N-methyl-α-β-ethylenpiperidine.

α-Ethylpiperidine and its Methyl Derivative.—A. Ladenburg.—These substances were prepared in a pure state, free from γ-ethylpyridine, by fractional distillation and re-crystallisation of the mercury salt, which boils at 147—150°.

N-methylpipecoline.—A. Ladenburg.—By reduction of the above substances with sodium and alcohol, N-methylpipecoline is formed, which was prepared, and some of its salts.

Action of Diazomethane on Aromatic Nitroso-Bases.—H. v. Pechmann and Wilhelm Schmitz.—The authors investigated the behaviour of diazobenzoyl towards aromatic nitroso-bases. First nitrosomethylaniline, and then nitrosoaniline, nitrosodiethylaniline, and *m*-oxynitrosodiethylaniline. The experiments showed that the reaction was similar to that between diazomethane and nitrosobenzol, glyoxim-N-phenyl ethers being formed, distinguished by their red colour and basic reaction.

Relations between Safranines and Isorosindulines and Rosindulines.—Otto Fischer and Eduard Hepp.

Action of Diazomethane and of Methyl Iodide and Potash on Nitrosophenol.—H. v. Pechmann and Eugen Seel.—Nitrosophenol and diazomethane react on one another with evolution of N, and from the reaction-products two substances can be isolated—chinonoximmethyl ether and paradioxyglyoxim-N-phenyl ether.

New Method of Preparing Tetrazin Derivatives.—A. Junghahn.—The author has prepared the derivatives of tetrazin by the action of hydrazin on the thiamides, the reaction being represented by the equation—

$$2R.CS.NH_2+2N_2H_4=$$
$$=2H_2S+2NH_3+R.C\begin{matrix}NH.NH\\ \diagdown\!\diagup\\ N-N\end{matrix}C.R.$$

Azimido Compounds of Benzimidazole.—St. von Niementowski.—By the action of HNO_3 on the *o*-amidobenzimidazoles, new compounds are formed which are true diazo-compounds. They form a homologous series of the general formula $C_nH_{2n-18}N_4$. A number of these were prepared and their properties investigated.

A Fluorescent Substance.—Br. Pawlewski.—When benzylchloride reacts with resorcin, the mixture being warmed on a water-bath, a fluorescent substance is formed. A red oily mass separates out, which, after many times extracting with boiling water and treating with aqueous alcohol, gives a red amorphous powder, which melts at 315—320°, and is difficult to analyse. It appears to have the formula $C_{26}H_{18}O_4$. It is not very soluble, and its alcoholic solution shows a green fluorescence, while an alkaline solution shows a red fluorescence, which on dilution becomes bright green.

MEETINGS FOR THE WEEK.

MONDAY, 16th—Society of Arts, 8. (Cantor Lectures). "Electric Traction," by Prof. Carus Wilson.

TUESDAY, 17th.—Royal Institution, 3. "The Historical Development of Modern Europe," by Samuel Rawson Gardiner, M.A., D.C.L., LL.D.

WEDNESDAY, 18th.—Society of Arts, 8. "The Evolution of the Cycle," by J. K. Starley.

— Microscopical, 7.30. Exhibition of Microscopic Aquatic Life.

THURSDAY, 19th.—Chemical, 8. "The Action of Formaldehyd on Amines of the Naphthalene Series," by G. T. Morgan, B.Sc. "On the Constitution of Oleic Acid and its Derivatives" (Part I.), by F. G. Edmed, B.Sc.

— Royal Institution, 3. "Heat," by The Right Hon. Lord Rayleigh, F.R.S., &c.

— Society of Arts, 4.30. "Chartered Companies and Colonisation," by Sir Alfred Comyns Lyall, G.C.I.E., K.C.B., D.C.L., Member of the Council of India.

FRIDAY, 20th.—Royal Institution, 9. "The Early Life and Work of Shakespeare," by the Rt. Hon. D. H. Madden, LL.D.

SATURDAY, 21st.—Royal Institution, 3. "The Biology of Spring," by J. Arthur Thomson, M.A.

MASON UNIVERSITY COLLEGE, BIRMINGHAM.

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(*c*) Three PRIESTLEY SCHOLARSHIPS in CHEMISTRY, each of the value of about £96.

The object of these Scholarships is to encourage higher work and research in Scientific Professional Engineering and in Chemical and Metallurgical Science.

Applications, supported by details of educational training and references to former teachers and others, should be sent to the Registrar on or before the 11th June, 1898. The awards will be made in September next, and the Scholarships will be tenable during the Session 1898-9.

Further particulars may be obtained on application to the REGISTRAR.

Young Man (20) desires situation as Assistant Chemist in Works. Has had three years with Public Analyst and two and a-half years College. Passed Final Exam. for the A.I.C.—Address, A. C., CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2008.

LIQUID HYDROGEN.

At the meeting of the Royal Society on the 12th inst. Professor Dewar contributed a preliminary note on the liquefaction of hydrogen and helium.

Professor Dewar said that in 1895 he described apparatus for the production of a jet of hydrogen containing liquid, and showed how such a jet could be used to cool bodies below the temperature that could be reached with liquid air, though all attempts to collect the liquid hydrogen failed. So far, no investigator had improved on the results described in 1895, and, as the type of apparatus employed in those experiments worked well, it was resolved to construct a much larger liquid air plant, and to combine with it circuits and arrangements for the liquefaction of hydrogen. The apparatus took a year to build up, and many months were occupied in testing and in making preliminary trials.

The many failures and defeats need not be detailed. On May 10 an experiment was started with hydrogen cooled to $-205°$ C., and escaping continuously under a pressure of 180 atmospheres from the nozzle of a coil of pipe at the rate of 10 to 15 cubic feet a minute, in a vacuum vessel doubly silvered, and of special construction, surrounded with a space kept below $-200°$ C. With these arrangements liquid hydrogen began to drop from this vacuum vessel into another, doubly isolated by being enclosed within a third, and in five minutes 20 c.c. of liquid were collected. The hydrogen jet then froze up from the solidification of air in the pipes of the apparatus. The yield of liquid was about 1 per cent of the gas. In the liquid condition the hydrogen was clear and colourless, showing no absorption-spectrum, and the meniscus was as well-defined as in the case of liquid air. The liquid must have a relatively high refractive index and dispersion, and the density must be in excess of the theoretical values, viz., 0·18 to 0·12, deduced respectively from the atomic volume of organic compounds and the limiting density found by Amagat for hydrogen gas under infinite compression. Professor Dewar's old experiments on the density of hydrogen in palladium gave a value for the combined body of 0·62, and it would be interesting to find the real density of the liquid substance at its boiling-point. No arrangements being at hand to determine the boiling-point, two experiments were made to prove the excessively low temperature of the boiling fluid. In the first place, when a long piece of glass tubing, sealed at one end and open to the air at the other, was cooled by immersing the closed end in the liquid hydrogen, the tube immediately filled, where it was cooled, with solid air.

The second experiment was with a tube containing helium.

The Cracow Academy *Bulletin* for 1896 contained a paper by Professor Olszewski entitled a "Research on the Liquefaction of Helium," in which he stated that, as far as his experiments went, helium remained a permanent gas, and apparently was much more difficult to liquefy than hydrogen. Professor Dewar, however, suggested that hydrogen and helium would probably be found to have about the same volatility, as was the case with oxygen and fluorine. Having a specimen of purified helium, extracted from Bath gas, sealed up in a bulb with a narrow tube attached, he placed the latter in the liquid hydrogen, whereupon a distinct liquid was seen to condense. From this result it would appear that there could not be any great difference in the boiling-points of hydrogen and helium.

In conclusion, Professor Dewar pointed out that all known gases had now been condensed into liquids which could be manipulated at their boiling-points under atmospheric pressure in suitably arranged vacuum vessels, though even so great a man as Clerk-Maxwell had doubts as to the possibility of ever liquefying hydrogen. With liquid hydrogen as the cooling agent, a temperature could be reached within 20° or 30° of the zero of absolute temperature, and its use would open up an entirely new field of scientific inquiry. No one could predict the properties of matter near that zero. Faraday liquefied chlorine in the year 1823. Sixty years afterwards, Wroblewski and Olszewski produced liquid air, and now, after an interval of fifteen years, the remaining gases—hydrogen and helium—were obtained as static liquids. Considering the step from the liquefaction of air to that of hydrogen was relatively as great in a thermo-dynamic sense as that from liquid chlorine to liquid air, the fact that the former had been achieved in one-fourth the time needed to accomplish the latter proved the greatly accelerated rate of scientific progress in the present age.

The paper ended with an acknowledgment of the aid rendered by Mr. Robert Lennox, without whose engineering skill, manipulative ability, and loyal perseverance the present successful issue might have been indefinitely delayed.

ON THE METALLIC PHOSPHIDES.

By A. GRANGER.

M. Albert Granger has recently published an important research on the metallic phosphides. After having made a critical examination of the attempts of his predecessors, he reviewed successively the different methods used for the preparation of compounds of metals with phosphorus; he then describes a certain number of these compounds. We here give the principal results obtained by him.

Preparation of Phosphides.

Action of Phosphorus on Metals.—By using the arrangement first designed by Schrötter, that is to say, by heating the metal under experiment, in a current of vapour of phosphorus carried by an inert gas, M. Granger was able to prepare a certain number of metallic phosphides; he also noted that some metals remained unattacked by phosphorus within a fairly wide range of temperature. The author thought it advisable to repeat nearly all the work of his prececessor, as much because of the uncertainty surrounding his results as on account of the meagreness of details contained in his memoir. It is plainly shown that if many of the compounds are disputable it is for two reasons only:—

1. A part of the metals submitted to experiment were not in a sufficiently pure state.

2. By not taking the precaution of cooling his apparatus rapidly in the vapour of phosphorus, the Viennese *savant* partially decomposed his phosphides. In fact, the current of gas at a still sufficiently low temperature might cause a loss of phosphorus, since the tension of dissociation could not be established, the atmosphere of the apparatus being unlimited. By taking the precaution of cooling the apparatus as rapidly as possible, and continuing the circulation of the current of phosphorus vapour over the still warm material, this loss of phosphorus can be avoided and pure crystalline phosphides can be obtained.

With metals, phosphorus forms bodies which may be considered as alloys of phosphorus and the metal, and which, by their peculiar properties, have been sometimes taken for definite compounds. Some of them even, by a species of pseudomorphism, are able to take not only the appearance of but even a crystalline form, which at first sight confounds them with other distinct compounds having a different composition.

Under the same conditions of temperature we always

find similar proportions of phosphorus; but in repeating the experiment, even very closely, we can always find small variations which are not met with in actual phosphides. Among these alloys we may mention Cu_3P and Fe_4P, first described by Abel and then by Sidot. While insisting on the action of phosphorus on these two bodies, we see that the quantity of the metalloid retained by the metal augments with the duration of the heating, and that it tends towards a limit established by a definite compound, which may be reached if the experiment be sufficiently prolonged. Thus the phosphide approaching Cu_3P at the temperature of formation can be transformed into a crystallised compound, Cu_5P_2, perfectly distinct, both in its physical and chemical properties, from alloys more or less resembling Cu_3P. By keeping subphosphide of iron in a melted state, phosphorus is given off, and M. Sidot believes that this shows not a decomposition but a purification of the body, by thus getting rid of the excess of phosphorus. By prolonging the time of heating, more or less, we obtain products more or less dephosphorised, and, amongst others, Fe_4P.

Before the time of Sidot another phosphide had already been described, Fe_3P. Freese acknowledges this in an extended work on phosphides of iron (*Pog. Ann.*, cxxxiii., 225), a work in which he shows that these much too numerous bodies are, for the most part, only mixtures.

Action of Phosphoretted Hydrogen on Metals.—This method of working, though adopted by several chemists, offers no advantage. At the temperatures to which one is obliged to carry the metals to effect the combination, sufficient phosphorus is set at liberty by the decomposition of the gas to make the operation practically the same as the former one, since we are only heating the metal in a vapour of phosphorus carried by an inert gas.

Action of Metals on Phosphoric Acid and the Phosphates, either alone or in the presence of Carbon.—Some experimenters have tried in vain to prepare phosphides by heating an oxidisable metal with phosphoric acid or a phosphate. By reason of the high temperature necessary to produce the reaction only bodies very poor in phosphorus can be obtained. By the addition of carbon, phosphorus is set at liberty, and is able to combine with the metallic element; but as it is still necessary to have recourse to a high temperature for a considerable time (which is a great drawback), we can only obtain satisfactory results in the very rare case of the phosphide being stable at a high temperature.

Reduction of Phosphates or Phosphites by Carbon or Hydrogen.—The reduction of phosphates and phosphites gives nothing but altered products. As it is necessary to operate at a high temperature, and to prolong the action of the reducing agent, the conditions are such as to render the decomposition of the phosphides at the moment of their formation a matter of great simplicity. It is, in fact, impossible to maintain an atmosphere saturated with the vapour of phosphorus, so that dissociation is extremely easy.

Action of Phosphoretted Hydrogen on some Metallic Compounds.—*A priori* it seems possible to isolate phosphides by passing phosphide of hydrogen over bodies such as chlorides, oxides, or sulphides of the metals. In practice it is of advantage to substitute the vapour of phosphorus for the phosphoretted hydrogen, when precisely the same reactions take place.

Action of Phosphoretted Hydrogen on Metallic Solutions.—There is complete dis-accord between the results obtained by different authors, but by repeating their experiments these discordances can be easily accounted for. Here several phenomena take place simultaneously; first of all the acid of the salt is set at liberty, and a precipitate of phosphide formed, which may be mixed with phosphorus, but, as the production of acid increases, there is a secondary reaction of the acid on the metallic phosphide and on the phosphide of hydrogen. The temperature and the degree of concentration of the solution are not without influence, so that as a result several reactions take place simultaneously, giving different results, and we can only procure very complex mixtures.

Action of Phosphorus on Metallic Salts in the presence of Water.—Nearly all salts give, under these conditions, mixtures of the metal and of phosphides which it is impossible to separate. In one particular case, however, by keeping phosphorus and phosphite of copper under water, pure crystallised cuprous phosphide could be seen forming.

Action of some Compounds of Phosphorus on Metals.—In face of the difficulties experienced in the experiments we have referred to, the author thought that it might be possible to isolate some phosphides by heating metals in the vapour of halogen compounds of phosphorus. With phosphorous chloride he did, in fact, obtain a chloride and a phosphide.

He has also experimented on the behaviour of the metals with the fluorides, bromides, and iodides of phosphorus. This method, however, is only applicable in the case when the combination of the metal with the halogen is soluble in a liquid without action on phosphorus.

Action of Phosphorus on some Metallic Compounds.—We can also make use of the reaction of phosphorus on the metallic chlorides for the preparation of phosphides; the phosphorus combines with the metal and eliminates the chlorine in the state of phosphorous chloride.

Action of Phosphorus and of Hydrogen on some Chlorides and Oxides.—Certain chlorides resist the action of phosphorus; but by making use of hydrogen at the same time, it has been possible to transform them into phosphides. This method of operating can also be applied to several oxides.

The Properties of the Phosphides.—Phosphides are solid bodies, generally possessed of a metallic lustre; they are all more or less decomposable by heat, so that when they are heated in a current of gas they are almost always partly decomposed. Chlorine and bromine attack them energetically, oxygen generally transforms them into phosphates. Certain phosphides—such as the sesquiphosphides of iron, nickel, and cobalt—are oxidised with difficulty, and resist the action of acids and of aqua regia.

Melted potash oxidises all the phosphides, as does also bromide potash. Mr. Granger has attempted to prepare alkaline phosphides, but he was stopped by the impossibility of separating the phosphide formed, either from the excess of phosphorus or from the excess of metal. These impure phosphides, prepared by direct action, are brownish bodies, of a waxy consistency, very inflammable, and decomposed by moisture.

Magnesium combines with phosphorus at about 600° with great ease; but at this temperature it attacks all substances in which it may be placed, so that it is impossible to isolate a pure product. Phosphide of magnesium is readily oxidisable, and decomposes on contact with water. Aluminium does not combine with phosphorus, at any rate not below 1000°.

Chromium unites directly with phosphorus at about 600°, and retains about 21 per cent, but the phosphoration is difficult to complete throughout the mass. It is a simple matter to prepare protophosphide of chromium by heating chromic chloride in a current of the vapour of phosphorus and hydrogen. The body, CrP, is of a greyish colour, and its structure is graphitoidal; it is not attacked by acids or by aqua regia.

Manganese at 700° absorbs about 24 per cent of phosphorus. But the difficulty of procuring this metal perfectly free from foreign matter prevents the isolation of pure compounds. A phosphide, Mn_3P_2, can be prepared in thin, brilliant flakes, in the same manner as phosphide of chromium.

Iron combines easily with phosphorus. We already know three phosphides, Fe_2P, FeP, and Fe_3P_4. By causing the trichloride to act on metallic iron, the author obtained Fe_4P_3, and afterwards, by heating ferric chloride in the vapour of phosphorus, he transformed it into sesquiphosphide, Fe_2P_3. These two phosphides are white in colour,

and crystallise in prismatic needles; they are not easily attacked, except by chlorine.

Nickel and cobalt, under the same conditions as iron, both form a subphosphide and a sesquiphosphide. Ni_2P exists as yellowish white crystals; Co_2P is white, in small, hard, and brilliant needle-like crystals; both are easily soluble in nitric acid. The subphosphides of nickel and cobalt resist the action of acids to the same extent as do the corresponding compounds of iron.

It was of interest to try whether with zinc, cadmium, and tin we could utilise the reaction of phosphorous chloride on the metal, or of phosphorus on the chloride, and prepare the compounds already known. The results were not satisfactory, as it was impossible to separate the products of the reaction without decomposing them.

Copper at 700° forms a subphospide of copper; then at about 900° another phosphide, Cu_5P_2. By heating either copper in the vapour of trichloride of phosphorus, or cuprous chloride in the vapour of phosphorus, a biphosphide of copper is formed. We have seen above how cuprous phosphide can be obtained.

Mercury does not unite directly with phosphorus. Heated with bi-iodide of phosphorus it forms a phosphide, Hg_3P_4, crystallising in hexagonal prisms, combined with the p and a' facets of a rhombohedron. Phosphide of mercury is easily decomposed under the influence of heat.

Lead, bismuth, and antimony do not combine with phosphorus directly, and all attempts to obtain such phosphides indirectly have only given amorphous bodies containing extremely small quantities of phosphorus.

Silver and chloride of silver form a biphosphide at 400°, when heated in a vapour of phosphorus. At 500° the biphosphide of silver decomposes, and gives off all its phosphorus if it is kept in a current of inert gas.

Gold behaves in the same way as silver; it combines with phosphorus at the same temperature, and gives Au_3P_4, which easily destroyed under the influence of heat.

Platinum is easily attacked by phosphorus; it gives extremely fusible compounds, and is very difficult to obtain crystallised. At 500° it forms a biphosphide; towards 600° a body less rich in phosphorus is formed, Pt_3P_5; above 700° a subphosphide is formed; and finally, at 1000°, the metal only retains a few hundredths of phosphorus.

The phosphides of platinum are attacked very slowly by aqua regia, but dissolve rapidly in melted alkalies.

Separation of Phosphoric Acid from the Metals.—To effect the separation of phosphoric acid from the metals, M. Granger has used electrolytic methods with success, in all cases where such a method was possible. Iron, nickel, zinc, cobalt, copper, cadmium, and tin, were very easily estimated, though the ordinary processes of analysis are sufficiently delicate. In nearly every case the phosphoric acid was precipitated in the form of ammoniomagnesic phosphate. In some cases the author used Chancel's reagent, and made the estimation in the form of phosphate of bismuth. The nitro-molybdic reagent has been used the least often for the separations, on account of the difficulty of freeing the liquor from the excess of molybdenum.—*Moniteur Scientifique*, Series 4, vol. xii., May, 1898.

THE ANALYSIS OF CAUSTIC SODA.

By P. DOBRINER and W. SCHRANZ.

The analysis of caustic soda includes the estimation of the caustic alkali and of the carbonate of soda. Two methods may be used for this analysis, The alkalinity may be determined before and after the elimination of the carbonate by chlorlde of barium, or the total alkalinity may be determined at the same time as the carbonic acid. In a series of comparative experiments we found that, according to the first method, the proportion of carbonate of soda present appeared to be from 1 to 2 per cent higher than the actual amount, and, naturally, the proportion of caustic soda would appear to be lower by the same quantity. We have shown that this error is due to the use of toughened folded filter-papers, for filtering the alkaline solutions treated by chloride of barium. These papers appear to absorb notable quantities of alkali. But if we use ordinary filter-papers this error disappears, and the two methods give concordant results. It is best to let the precipitated carbonate of baryta settle thoroughly, and to use a definite known quantity of the clear liquid for the determination of the caustic alkali. Results of sufficient accuracy can be obtained by the following method:—

To 2·65 grms. of caustic soda dissolved in 50 c.c. of water, add phenolphthalein, and titrate with normal sulphuric acid until the red colour disappears. Then add 3 c.c. more of the normal acid, and boil for five minutes to drive off the carbonic acid; then titrate the excess of acid by normal soda.

If a be the number of c.c. of normal acid used in the first titration, and b the number of c.c. of normal soda used in the second titration (after driving off the carbonic acid), then the proportion of caustic soda present will be $2(2a-b)$ per cent Na_2CO_3, corresponding to NaHO and $4(b-a)$ per cent Na_2CO_3.

It is well known that this method is based on the fact that, in the first titration, the whole of the caustic alkali is neutralised, and half the carbonate transformed into bi-carbonate—

$$NaHO + Na_2CO_3 + H_2SO_4 = Na_2SO_4 + NaHCO_3.$$

This reaction has served as the starting-point for a large number of methods for the estimation of caustic alkalis in presence of the carbonate; but these methods only give exact results when the quantity of carbonate present is very small.

Lunge recommends titrating first with phenolphthalein as indicator, until decolouration takes place, and then to continue with methyl-orange as indicator. Those chemists who do not like the use of methyl-orange as an indicator will find the method we propose very convenient.—*Zeitsch. fur Angewandte Chemie*, xiv., 455.

ON THE YTTRIC EARTHS CONTAINED IN THE MONAZITE SANDS.*

By P. SCHÜTZENBERGER and O. BOUDOUARD.

(Concluded from p. 221).

B.—The oxides of which the atomic weights of the corresponding metals are 104·55, 104·65, and 104·2 were mixed and converted into nitrates. The method of fractional fusions gave:—

Sub-nitrate No. 1.

Atomic weight	107·95
Anhydrous sulphate used	2·7597
Oxide obtained	1·4453

Sub-nitrate No. 2.

Atomic weight	105·6
Anhydrous sulphate used	2·0655
Oxide obtained	1·0725

Sub-nitrate No. 3.

Atomic weight	102·2
Anhydrous sulphate used	1·3767
Oxide obtained	0·7058

Mother-liquors.

Atomic weight	103·0
Anhydrous sulphate used	4·8470
Oxide obtained	2·4930

* *Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 6.

This last oxide, transformed into nitrate, was heated up to 325° and submitted to a partial decomposition :—

Sub-nitrate No. 1.

Atomic weight	101·25
Anhydrous sulphate used ..	1·0577
Oxide obtained	0·5402

Mother-liquors.

Atomic weight	102·45
Anhydrous sulphate used ..	3·4885
Oxide obtained	1·7900

C.—The oxide previously obtained, which gave 97·1, was converted into nitrate and submitted to a partial decomposition at 325°.

Sub-nitrate No. 1.

Atomic weight	104·5
Anhydrous sulphate used ..	1·1355
Oxide obtained	0·5873

Sub-nitrate No. 2.

Atomic weight	101·75
Anhydrous sulphate used ..	1·0865
Oxide obtained	0·5560

Mother-liquors.

Atomic weight	95·1
Anhydrous sulphate used ..	3·0125
Oxide obtained	1·5005

The oxides of which the atomic weights were respectively 97·45, 97·7, and 97·5 were dissolved in nitric acid. The nitrate was then partially decomposed :—

Sub-nitrate No. 1.

Atomic weight	103·8
Anhydrous sulphate used ..	1·6036
Oxide obtained	0·8271

Sub-nitrate No. 2.

Atomic weight	98·5
Anhydrous sulphate used ..	1·1945
Oxide obtained	0·6036

Sub-nitrate No. 3.

Atomic weight	95·6
Anhydrous sulphate used ..	0·8465
Oxide obtained	0·4225

Mother-liquors.

Atomic weight	96·0
Anhydrous sulphate used ..	2·5795
Oxide obtained	1·2895

D.—We united all the oxides having given 122, which represents 5·95 grms. The nitrate was submitted to partial decomposition at 325°. We obtained three sub-nitrates and an undecomposed portion, which were analysed.

Sub-nitrate No. 1.

Atomic weight	142·0
Anhydrous sulphate used ..	3·1217
Oxide obtained	1·8132

Sub-nitrate No. 2.

Atomic weight	126·0
Anhydrous sulphate used ..	2·2050
Oxide obtained	1·2250

Sub-nitrate No. 3.

Atomic weight	117·8
Anhydrous sulphate used ..	0·9655
Oxide obtained	0·5230

Mother-liquors.

Atomic weight	110·15
Anhydrous sulphate used ..	4·2022
Oxide obtained	2·2182

We now wished to find out if the oxide giving 142 was a final term. Transformed into nitrate and submitted to a partial decomposition at 325°, it gave an insoluble sub-nitrate and an undecomposable portion.

Sub-nitrate No. 1.

Atomic weight	155·75
Anhydrous sulphate used ..	0·9855
Oxide obtained	0·5910

Mother-liquors.

Atomic weight	137·4
Anhydrous sulphate used ..	1·6968
Oxide obtained	0·9733

This last oxide, after solution in nitric acid, was decomposed afresh.

Sub-nitrate No. 1.

Atomic weight	150·2
Anhydrous sulphate used ..	0·7720
Oxide obtained	0·4570

Mother-liquors.

Atomic weight	123·25
Anhydrous sulphate used ..	0·8863
Oxide obtained	0·4884

Finally, the oxides 155·75 and 150·2 were united, transformed into nitrates, and submitted to a fresh partial decomposition.

Sub-nitrate No. 1.

Atomic weight	162·5
Anhydrous sulphate used ..	0·6425
Oxide obtained	0·3910

Mother-liquors.

Atomic weight	148·3
Anhydrous sulphate used ..	1·0500
Oxide obtained	0·6190

In face of the small quantity of material at our disposal, we were unable to continue our research, and so make quite sure that we had not reached the highest limit of decomposition. As the atomic weights of holmium, ytterbium, and erbium are in the neighbourhood of 165, we thought this should be the ultimate term. All the products having given intermediate atomic weights should therefore be considered as mixtures of these earths with high atomic weights with an earth having a considerably lower one; this latter, however, being quite distinct from yttrium. Yttrium (89·5) is not found in the monazite sands, except in very minute proportions; we have never in the course of these determinations been able to isolate more than a very small quantity of yttria (4 to 5 grms. of oxides having an atomic weight of from 93 to 94).

In spite of this great diversity in the atomic weights determined by a method so simple that an error is hardly possible, all these earths give a spark spectrum with the chloride similar to, and easily confounded with, that of the original mixture. This spectrum, above all, shows two characteristic shadowy bands to the left, formed by the juxtaposition of the lines occupying—(*a*) the space comprised between numbers 69 and 73 on the micrometer scale of our instrument, in which division 90 coincides with the sodium D line—

$$\lambda = 618 \text{ to } 614;$$

and (*b*) the space comprised between the divisions 80 and 85—

$$\lambda = 602 \text{ to } 595{\cdot}5.$$

We have further noticed, but in a less marked manner, other lines, of which the most apparent are—(*c*) those comprised between the divisions 188 to 190—

$$\lambda = 499 \text{ to } 497{\cdot}5;$$

and (*d*) those comprised between the divisions 217 to 220—

$$\lambda = 481{\cdot}5 \text{ to } 480.$$

In conclusion, the spectra observed seem to be confounded with that of yttrium, and the conclusion to which one is led by spectrum analysis would certainly be that the earths examined by us are almost pure yttria, at

the most contaminated by only a few hundredths of foreign earths.

In a future paper I shall give the results at which I arrived by continuing the study of the yttric earths.

A REVISION OF THE ATOMIC WEIGHT OF ZIRCONIUM.*

By F. P. VENABLE.

(Concluded from p. 223).

Method of Work.

The purified chloride was introduced into a small glass flask having a capacity of 100 c.c. This was provided with a glass stopper ground to fit, and also a second one with two tubes arranged for the passage of the hydrochloric acid gas. The arrangement of the tubes was similar to that in an ordinary ether wash bottle, though both tubes outside were bent downwards and had little bulbs blown in them for catching moisture, &c. A Thorner bath was found to be very convenient for keeping these flasks at 100° C. The hydrochloric acid was prepared by allowing sulphuric acid to drop into a large flask containing the hydrochloric acid. The gas thus obtained in a regular stream, was passed through a wash-bottle containing sulphuric acid and then through towers filled with glass beads kept moist with concentrated sulphuric acid.

The drying took from fifty to one hundred hours (in some extreme cases). If the stream of gas was rapid the temperature could rise to 110° or even higher without decomposition of the chlorine. A much lower temperature caused this decomposition if the stream was insufficient to keep the flask full of gas. A number of experiments were carried out showing these facts. Indeed, two in the series of determinations were lost by the stream of gas becoming too slow or altogether ceasing for a short while (Experiments VI. and VIII.). It was thought from experiments at first that where this decomposition had begun it was impossible to secure a constant weight of the residue, but this is certainly not true where the decomposition has been only slight. Of course, this introduces a chance for error in the method. The drying must be watched quite closely, and not more than eight or ten hours of drying could be easily managed in a day.

At first it was feared to remove the atmosphere preparatory to weighing, and efforts were made at weighing the flasks full of hydrogen chloride. These results were too low and varied among themselves, so that it was evidently impracticable to carry out the experiments in this way. It was found that the hydrochloric acid could be replaced by dry air. The flask was removed from the bath, and dry pure air passed through it for half an hour. It is, of course, essential that the air be carefully dried. The tubes are then removed and the glass stopper quickly fitted in its place. It is then ready for placing in the balance case. The chloride is deliquescent and some trouble in weighing was experienced. If the stopper was well ground there was no appreciable change in the weight in from twenty to forty minutes after placing upon the balance. The loss of weight in the latter part of the drying was very slow. The weighings were taken at intervals of from six to eight hours' heating. The number of weighings necessary before constancy was secured served as a safeguard against error. A series of such weighings is given further on.

After drying, the chloride was dissolved in a small amount of water (re-distilled) and this solution, with rinsings, transferred to a platinum crucible. It was evaporated to dryness upon a water-bath, with due precautions against dust, &c.; was next heated gradually upon a sand-bath until most of the chlorine had been driven off, and was then slowly raised to the highest temperature attainable by the Bunsen burner. During this latter part of the operation the cover was kept on. Three or four days were thus consumed, the gradual heating giving a coherent flinty mass of glistening semi-translucency which could be safely heated by the water-blast without loss. During the driving off of the chlorine the platinum crucible was more or less attacked, but as this was before the lid was on, there was little chance of loss from this source. This corroded platinum was probably the reddish brown decomposition product mentioned by Bailey as coming from the ignition of the oxychloride.

The last of the chlorine was driven off by heating with a water-blast for from forty-five to seventy hours. The last weighings were made at intervals of from six to twenty hours, and were recorded as constant if they agreed within 0·00005 of a grm. A series of weighings is here given as an example. Experiment No. II., or the first one successfully carried out in the series, is taken for the purpose.

Weights of zirconium chloride—March	28	5·25910
,, ,, ,,	29	5·25786
,, ,, ,,	30	5·25760
,, ,, April	1	5·25762
Weights of zirconium oxide—April	11	2·78759
,, ,, ,,	12	2·78724
,, ,, ,,	13	2·78583
,, ,, ,,	15	2·78517
,, ,, ,,	16	2·78452
,, ,, ,,	17	2·78451

This zirconia was examined for chlorine in most of the analyses and was found to be free from it. In the last three experiments reported in the series, the ignited residue was treated with hydrofluoric acid. Ignition after this treatment was very difficult, as the mass was not compact and coherent. The finely-divided zirconia was lost in spite of the most careful treatment. The first was lost altogether and the weighing was not carried out. The second showed upon the lid signs of the powdered zirconia having been swept out. The total loss of weight, however, was less than 1 m.grm. This could readily be attributed to the zirconia and pointed to the absence of silica, unless in insignificant traces.

I think great purity may be claimed for the preparations used in the analyses. Crystallising from hot hydrochloric acid is apt to remove most known impurities, and they were eliminated beyond the possibility of detection by the ordinary tests. The analyses were not made from the same preparation, but from small quantities prepared at different times, and some crystallised ten or a dozen times more than others, yet no appreciable difference could be detected in the results. That these results are not in close accord with one another, is due in part to the deliquescence of the chloride and to the risks involved in the prolonged heating of the oxide.

Sources of Error.

Five main sources of error have occurred to me apart from any question as to the purity of the material.

1. The deliquescence of the chloride.
2. The loss of the finely-divided zirconia.
3. The corrosion of the platinum crucibles.
4. The attack of the glass flasks by the gaseous and liquid hydrochloric acid. It is very evident that the glass vessels would suffer when subjected to the action of hydrochloric acid during such prolonged periods. The weighings easily revealed the extent of this action; it was found to vary with different flasks. For instance, flask I. lost 0·00116, 0·00031, 0·00023, and 0·00078 grm. On the other hand, flask IV. weighed after the first experiment only 0·00011 grm. less, and after the next two experiments the loss was 0·00013, and the total loss during three experiments was 0·00024. This is probably trans-

* From the *Journal of the American Chemical Society*, xx., No. 2.

ferred mainly as alkaline chlorides to the crucibles, and is there volatilised. Sodium could readily be detected upon the lid of the crucible after partial ignition. Of course, if all is volatilised then no error is introduced into the experiment, but there may be some non-volatile material also transferred from the flasks. The total amount is so small that the error cannot be a large one.

5. Substances carried into the drying flasks by the stream of gas. Much care was taken to avoid error from this source. The main danger lay in the necessity for the use of some rubber connections. Vulcanised rubber was used. It was freed from excess of sulphur and was replaced by fresh pieces when attacked by the gas. The dry gas does not attack rubber very rapidly. Gaseous sulphur compounds, coming from the sulphuric acid used in preparing and drying the hydrogen chloride, were probably carried through the drying flasks, but there seems to be no probability of their causing a decomposition of the oxychloride.

The Determinations.

All analyses which were completed under the proper conditions of the method, as already given, are here reported. Experiment III. became contaminated from the iron support during the prolonged heating, and came out consequently a little high, giving the ratio of $ZrO_2 : ZrOCl_2.3H_2O$ as 53·12. In most of the subsequent analyses the ignition was carried out with the the crucible suspended in a platinum wire cage from a glass support. Experiments VI. and VIII. were dried with an insufficient stream of gas, as already stated, and hence were partially decomposed; they gave 53·57 and 53·8 respectively. The remaining analyses follow:—

	$ZrOCl_2.3H_2O$.	ZrO_2.	Ratio.
II.	5·25762	2·78450	52·961
IV.	5·53994	1·87550	52·981
V.	3·25036	1·72435	53·051
VII.	1·52245	0·80708	53·012
IX.	2·98802	1·58274	52·969
X.	2·11371	1·11920	52·949
XI.	2·38139	1·26161	52·978
XII.	1·90285	1·00958	53·055
XIII.	2·61847	1·38658	52·954
XIV.	1·07347	0·56840	52·951
	26·64828	14·11953	52·986

Calculating these for the ratio $ZrOCl_2.3H_2O : ZrO_2$, taking H=1·008, O=16, and Cl=35·45, we have the following:—

Maximum ratio ..	53·055	Atomic weight ..	91·12
Mean ,, ..	52 986	,, ,, ..	90·78
Minimum ,, ..	52·951	,, ,, ..	90·61

The atomic weight, as determined by Bailey, is 90·65. The mean value given in Clarke's "Re-calculation" is 90·40. I purpose repeating the determinations with the oxychloride, with such modifications as have occurred to me since the completion of the above work.

Estimation of Phenylhydrazin.—M. Causse.—0·20 grm. of hydrochlorate of phenylhydrazin is placed in a 500 c.c. flask, and 60 c.c. of a special solution of arsenic is added. (This solution is made by adding 125 grms. of arsenic acid to 450 grms. of water and 150 grms. of HCl, filter, and make up to a litre with glacial acetic acid). The flask, fitted with a vertical condenser, is gently heated; after 40 minutes add 200 c.c. of water, neutralise with soda until distinctly alkaline to phthalein, re-acidulate with HCl, and add, when cold, 60 c.c. of bicarbonate of soda (saturated), 3 to 4 c.c. of starch water, and titrate with a decinormal solution of iodine (1 c.c. = 0·0127 I).—*Bull. Soc. Chim. de Paris*, Series 3, vol. xix.-xx., No. 4.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 10th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined by us, all were found to be clear, bright, and well filtered.

We have once more to record a deficiency in the rainfall at Oxford, though not so serious a one as last month; the actual fall during the month of April was 1·34 inches and the thirty years' average 1·66 inches, leaving a deficiency of 0·32 inch. This brings the total deficiency for the year to 3·07 inches.

Our bacteriological examinations of 237 samples have given the results recorded in the following table; we have also examined 34 other samples, from special wells, standpipes, &c., making a total of 271 in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	611
New River, filtered (mean of 23 samples) ..	10
Thames, unfiltered (mean of 24 samples) ..	7854
Thames water, from the clear water wells of five Thames-derived supplies (mean of 118 samples)	17
Ditto ditto .. .. highest	231
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	2070
River Lea, from the East London Company's clear water well (mean of 24 samples) . ..	24

As we pointed out last month, the continued small rainfall in the Thames valley has had a very beneficial effect on the quality of the water; both the bacteriological results in the table above, and the comparative chemical results in the following table, show this in a marked manner. The quality of the water is in every respect excellent:—

Comparison of the Averages of the Five Thames-derived Supplies for the Months of April, 1897 and 1898.

	Common Salt. Per gall. Means.	Nitric Acid. Per gall. Means.	Hardness. Degrees. Means.	Oxygen. reqd. Per gall. Means.	Organic Carbon. Per gall. Means.	Organic Carbon. Per gall. Max.	Colour. Br'n: Blue. Means.
April,							
1897.	2·030	1·020	15·99	0·043	0·097	0·129	9·0 : 20
1898.	2·165	0·775	14·83	0·032	0·074	0·109	10·1 : 20

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 5th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. E. C. Jee, W. Marshall, and T. H. Pope, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harry Brearley, Totley, Derbyshire; Arthur Stanley Hemmy, Government College, Lahore; Leonard Myddleton Nash, 281, Seven Sisters' Road, Finsbury Park, N.; Edward John Russell, Owens' College, Manchester; Sigmund Stein, 323, Vauxhall Road, Liverpool; Frank Edwin Weston, 43, Larkhall Rise, Clapham, S.W.; William Williamson, 86, Tyndall Road, Leyton, N.E.; Charles Arthur Wrench, 3, Parklands, Surbiton Hill.

Of the following papers those marked * were read:—

*69. "*The Action of Hydrogen Peroxide on Carbohydrates in the presence of Iron.*" By C. F. Cross, E. J. Bevan, and Claude Smith.

The results obtained by H. J. H. Fenton (*Trans.* 1894, lxv., 899; 1895, lxvii., 48; 1896, lxix., 546) in oxidising tartaric acid by hydrogen peroxide in presence of soluble iron compounds suggested the application of the method to other hydroxy-compounds, and notably to the carbohydrates. The authors have studied the behaviour of typical hexoses and of cane-sugar, when treated in aqueous solution with hydrogen peroxide at ordinary temperatures, and, in confirmation of Fenton's observations, have found in this group also that the presence of iron compounds is an essential condition for the production of the characteristic reactions. A convenient proportion of iron (Fe as $FeSO_4 \cdot 7H_2O$) is 1/10000 of the weight of a solution containing 4 grms. of the carbohydrate in 100 c.c. The authors reserve for the present any statement of the limiting proportion which may be necessary, and are engaged in ascertaining whether other inorganic compounds may not be found to have similar effects.

With such proportions and with hydrogen peroxide in quantities sufficient to supply 1 or 2 atoms of oxidising oxygen for each molecule or hexose, reaction takes place readily with marked rise of temperature (10—20°), but in the absence of iron compounds, all other conditions remaining the same, nothing happens at ordinary temperatures. After reaction the solutions are acid to the taste. The quantity of acid formed is greater from dextrose than from lævulose. The volatile acids separated by distillation are formic and acetic acids, and represent 15—20 per cent and 4—7 per cent respectively of the weight of the dextrose. The non-volatile acids represent about one-half the total acidity, and contain a dicarboxylic acid which is easily isolated by precipitation as lead salt in the presence of acetic acid, and on analysis gives numbers corresponding with those required for tartronic acid.

After removal of the acids, the presence of furfuroids is identified by estimations of furfural in the distillates from hydrochloric acid (sp. gr. 1·08). The quantities obtained from dextrose or cane-sugar are 3—4 per cent, representing 7—9 per cent of the furfuroid. The products yielding furfural are not acid in character, but there is no evidence that they are pentoses. From lævulose, only traces of these products are formed. The solutions give a well-marked iodoform reaction, indicating that the hexose molecules undergo internal re-arrangement, and that the phenomena are not those of a simple oxidation.

The characteristic products of the reaction are separated from solution by the addition of alcohol and ether; on drawing off the denser aqueous layer, a solution is obtained which dries in a vacuum to a gummy solid, destitute of any appearance of crystallisation. These compounds react with phenylhydrazine acetate in the cold, forming osazones, and give evidence of the presence of highly reactive groups by reducing Fehling's solution in the cold. The yield of osazones is considerable, amounting to 30—60 per cent of the weight of the carbohydrate in the case of lævulose and of cane-sugar, and to 12—20 per cent in that of dextrose. Two groups of osazones have been obtained:—(1) compounds melting at 185—195°, and resembling the glucosazones in properties, but differing from them in composition, the nitrogen (N = 17—20 per cent) being 2—3 per cent higher; (2) compounds with a low melting-point (130°), and freely soluble in hot water. From these results it might be inferred that the products are the "osones" or "oxyglucoses" of Fischer, but they resist the action of zinc and acetic acid on the one hand, and of bromine on the other, and are not reduced by sodium amalgam in solutions kept slightly acid,—properties which differentiate them from the normal carbohydrates and from such of their oxy-derivatives (ketaldoses) as are at present known.

The investigation of the nature of these products is complicated by the fact that no crystalline derivatives other than the osazones have been obtained. No definite acetates or benzoates have been isolated. Some evidence as to their relationship to the original hexoses, however, is obtainable from a closer study of the constants of the reaction. It appears, in the first place, that there is no simple proportion between the quantity of hydrogen peroxide employed and the amount of the characteristic products obtained. Having established this for quantities representing 3, 2, and 1 atoms of oxygen for each molecule of the hexose, the authors found that very considerable effects were still produced on further reducing the proportion of peroxide. Thus from 40 grms. dextrose treated with sufficient peroxide to furnish only 1/10 atom of oxygen for each molecule of hexose, the quantity of osazones formed in the cold from the product of the reaction was 8 grms., an amount as great, therefore, as that obtained when ten times this proportion of the peroxide was employed. Similarly, the addition of still smaller quantities of the peroxide to a dextrose solution was found to convert a considerable proportion of the hexose into compounds not fermented by yeast, though reducing Fehling's solution and otherwise resembling the compounds just described.

The authors conclude (1), that hydrogen peroxide acts primarily by determining a constitutional change in the hexose molecule, *i.e.*, by internal re-arrangement, such effects bearing no direct proportion to the quantity added; and (2), that the oxidising actions observed—*e.g.*, the formation of dicarboxylic acids—are subordinate or secondary effects.

As regards the nature of the constitutional changes in question, the reactions of the characteristic products indicate the presence of $-C(OH):C(OH)-$ groups. In the formation of dihydroxymaleic acid from tartaric acid, this radicle results from an actual removal of hydrogen by oxidation, and in the carbohydrates might be formed by internal re-arrangement. The authors consider that such a change is the primary effect of contact with the peroxide, although $-CH(OH)\cdot CH(OH)-$ residues also are probably attacked and hydrogen eliminated by direct oxidation.

The obvious bearings of these results upon the problem of plant physiology, from which point of view they are positive and sufficiently established, induce the authors to put forward this preliminary communication without waiting for a definite solution of the constitutional problems, which are still under investigation.

Discussion.

Dr. Armstrong referred to the interest of the work in connection with vegetable physiology, indicative as it was of the far-reaching character of the interactions concerned in the elaboration of the products of plant activity. Although the part played by enzymes in such processes

had been generally recognised, their importance must be much accentuated now that Buchner's remarkable discovery of an enzyme capable of inciting alcoholic fermentation was placed beyond doubt. It seemed quite possible, from the experiments of Mr. Cross and his colleagues, that iron, which is known to be present in most plants, may behave to some extent as an enzyme, and thus possess unexpected importance from the point of view of plant chemistry; it was very noteworthy from this point of view that the formation of reduction products yielding iodoform had been observed as well as that of oxidation products.

Dr. Morrell stated that, with galactose, the disappearance of hydrogen peroxide is twice as rapid as with glucose, and that the addition of large quantities of the peroxide caused a marked rise of temperature. Ferrous iron, which could not be detected during the oxidation, reappeared when hydrogen peroxide could be recognised no longer in the solution.

Mr. Fenton said that, since he had observed the peculiar influence of iron in the oxidation of tartaric acid, experiments had been made in other directions, and as so wide a field had been opened up for investigation the co-operation of the authors and of Dr. Morrell was most welcome.

Mr. Ling, referring to the possible analogy between the products of the reaction described by the authors and those formed by the oxidation of sugars by alkaline copper solutions, said that Kjeldahl had observed that glucose and fructose, when boiled with a solution of potassio-copper sulphate (Ost's solution), yield mesoxalic acid. Kjeldahl had also shown that this acid, on treatment with phenyl-hydrazine acetate, is converted into a dihydrazide melting at 148°,—a derivative, therefore, of dihydroxymalonic acid. Might not the supposed osazone, which was formed in the cold, be a substance of this kind?

Mr. Cross, in reply, stated that the phenylhydrazine derivatives obtained in the cold had the characteristics of osazones, although neither aniline nor ammonia, which, according to Fischer, are simultaneously produced in the osazone reaction, could be detected in the filtrates. It had not escaped attention that the derivatives might possibly be hydrazides resulting from condensation with a $-C(OH):C(OH)-$ group, and they were being investigated from this point of view.

*70. "*Note on the Oxidation of certain Acids in presence of Iron.*" By Henry J. Horstman Fenton, M.A.

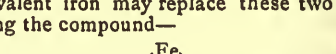
It has been shown in several previous communications (*Trans.*, 1894, lxv., 899; *B. A. Report*, 1895, &c.) that when tartaric acid is oxidised in presence of a small quantity of ferrous iron, 1 molecule of the acid loses 2 atoms of hydrogen, giving rise to dihydroxymaleic acid. The most effective oxidising agent for the purpose is hydrogen dioxide, but the result is also brought about by chlorine, hypochlorites, bromine, &c., and by atmospheric oxygen in presence of sunlight. The presence of ferrous iron is essential, but its proportion seems to bear but little relation to the yield of acid in the ordinary course of preparation, the action being, in fact, what is usually termed catalytic. It is necessary that the addition of iron shall precede that of the oxidising agent. From the fact that dihydroxymaleic acid, on heating with water, yields glycollic aldehyde, and that this readily condenses to a hexose, it is evident that the change may afford information with regard to the natural formation of carbohydrates.

The production of dihydroxymaleic acid from tartaric acid is most easily represented by assuming the removal of the two non-hydroxylic hydrogen atoms—

$$C_2H_2(OH)_2(CO_2H)_2 - H_2 = C_2(OH)_2(CO_2H)_2.$$

It is true that dextrotartaric acid would be expected, in this manner, to yield a fumaroid instead of a maleoid acid, but it is quite possible that "stereomeric" change takes place during one of the stages of preparation, and in any case this objection can hardly be considered a serious one, bearing in mind the large number of known exceptions (Michael, *J. Prakt. Chem.*, 1892, xlvi., 400).

While seeking for a chemical explanation of the part played by the iron, the following may be offered as a provisional suggestion. The two non-hydroxylic hydrogen atoms in tartaric acid may be supposed to possess feebly acid functions owing to the neighbourhood of the CO_2H- and $OH-$ groups, and it is possible that an atom of divalent iron may replace these two hydrogen atoms, giving the compound—



On addition of the oxidising agent the iron atom assumes the trivalent state, and can therefore no longer be "retained." The result is an unsaturated acid, and the iron enters into solution as a ferric salt, *e.g.*, ferric tartrate. Dihydroxymaleic acid readily reduces ferric salts in the cold, experiment indicating that 2 atoms of iron are reduced by 1 molecule of the acid, so that the ferrous iron is regenerated at the expense of a portion of the acid.

A large number of the commoner acids have been investigated as regards their behaviour in this respect. In addition to all the non-hydroxylic acids examined, lactic, malic, citric, and tartronic acids give negative results. If, however, the above explanation be accepted, it is evident that the production of the violet colouration would only be expected in the case of those acids the molecules of which contain at least two $CH(OH)-$ groups. Mucic and saccharic acids might therefore be expected to yield positive results, and recent experiments have shown that this is the case. Both these acids, when treated in the cold with a limited quantity of hydrogen dioxide in presence of ferrous iron, give intense violet colourations. Attempts are being made to isolate the oxidation products, which appear to be even less stable, however, than dihydroxymaleic acid.

Discussion.

Dr. Armstrong thought a more probable explanation of the part played by iron to be that the iron salt became added to the carboxylic group; if changes then occurred such as he had suggested take place when optical inversion is effected by hydrolytic agents (*Trans.*, 1896, lxix., 1399), it would be easy to understand why dihydroxymaleic acid was obtained instead of the fumaric derivative.

Mr. Fenton, referring to the suggestion he had made, said that replacement of non-hydroxylic hydrogen atoms by metals might also occur in Fehling's and other similar solutions. In experiments with equal molecular quantities of dihydroxytartrates and tartrates, it had been found that the power of retaining copper in solution in the presence of alkali is very much greater in the latter case, although the reverse might be expected if replacement occurs in the alcoholic hydroxyl groups as is commonly supposed.

*71. "*Properties and Relationships of Dihydroxytartaric Acid.* Part II. *Metallic Salts.*" By Henry J. Horstman Fenton, M.A.

The only metallic dihydroxytartrate which appears to have been prepared and studied is the sodium salt—the supposed barium salt being probably a mixture. Several other salts of the acid are now described. It is shown that the solubilities of the normal salts of sodium, potassium, rubidium, and cæsium increase with the rise in atomic weight of the metal. The lithium salt is exceptional, its solubility being greater than that of the sodium salt. The differences in solubility of these salts may perhaps be of service in separating the metals of the alkalis.

Solutions of soluble dihydroxytartrates act as powerful reducing agents towards salts of silver, copper, and mercury, but are themselves reduced to dihydroxymaleic acid by stannous and ferrous salts.

72. "*The Affinity-constants of Dihydroxymaleic, Dihydroxyfumaric, Dihydroxytartaric, and Tartronic Acids.*" By S. Skinner, M.A.

The affinity-constants have been determined from the conductivity of the aqueous solutions. The determination in the case of these acids, with the exception of tartronic acid, presents special difficulty as their solutions undergo gradual decomposition. The constants found are compared with those of malonic, succinic, fumaric, maleic, and tartaric acids, and it is shown that an increase in the value of the constant occurs—(1) on the introduction of hydroxyl groups; (2) for the lower members of the series of dibasic acids; (3) for the unsaturated acids as compared with their saturated isologues.

Discussion.

Dr. Wallace Walker objected to the explanation given of the nature of the curves, on the ground that in the production of carbon dioxide and glycollic aldehyde from dihydroxymaleic acid, the concentration of the supposed catalyser is decreasing at the same rate as that of the negative ion. The reaction would therefore be bimolecular, and its curve not rectilinear but one represented by an equation of the second degree.

Mr. Fenton asked whether the results obtained with dihydroxymaleic acid could be explained by the suggestion, advanced in a previous communication, that combination with a molecular proportion of water occurs on dissolution with the production of the unstable trihydroxysuccinic acid.

Mr. Skinner, in reply, recognised that explanations of the behaviour of dihydroxymaleic acid other than that adopted in the paper were possible, but he was not prepared to say how far they would be of assistance in elucidating the results of the conductivity experiments.

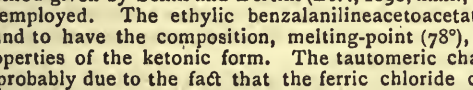
*73. "*Note on the Enolic and Ketonic Forms of Ethylic Acetoacetate.*" By R. S. Morrell, M.A., Ph.D., and J. M. Crofts, B.A., B.Sc.

The authors find that the purple oil obtained by the action of anhydrous ferric chloride on ethylic acetoacetate is decomposed by water in the presence of ether into ferric chloride and the ketonic ethereal salt. The ether is found to contain the ketonic and not the enolic form, as would be expected. To identify the ketonic form, the method given by Schiff and Bertini (*Ber.*, 1898, xxxi., 207) is employed. The ethylic benzalanilineacetoacetate is found to have the composition, melting-point (78°), and properties of the ketonic form. The tautomeric change is probably due to the fact that the ferric chloride compound of ethylic acetoacetate, when decomposed by water in the presence of ether, produces hydrochloric acid, which converts the enolic into the ketonic form.

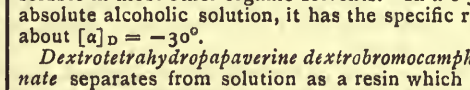
The authors mentioned in a previous paper that ethylic benzaldiacetoacetate formed a purple oil with ferric chloride in benzene solutions, whereas in alcoholic solution there was no such colouration. This oil has been obtained in the solid form, and is being investigated on the lines just indicated for the ethylic acetoacetate compound.

*74. "*The Resolution of Tetrahydropapaverine into its Optically Active Components.*" By William Jackson Pope and Stanley John Peachey.

Goldschmiedt has shown that papaverine is optically inactive, and is, in all probability, an isoquinoline derivative of the constitution—



This formula does not contain an asymmetric carbon atom, and, up to the present, no optically active derivative of papaverine has been described. Amongst the derivatives of papaverine prepared by Goldschmiedt (*Monats.*, 1886, vii., 495) is a tetrahydropapaverine, $C_{20}H_{25}NO_4$, to which, on the basis of the above constitution, the formula



must be assigned, since, on reducing isoquinoline derivatives, hydrogenation takes place in the pyridine nucleus. On this assumption, tetrahydropapaverine contains an asymmetric carbon atom, and it should therefore be possible to separate the optically inactive compound into two enantiomorphously related isomerides, and thus obtain evidence confirming the constitution which Goldschmiedt has assigned to papaverine.

In "splitting" an externally compensated base into its enantiomorphously related components, the dextrotartrate is almost invariably employed; it would seem preferable, however, on various grounds, to make use in such cases of the dextrobromocamphorsulphonic acid described by Kipping and Pope (*Trans.*, 1893, lxiii., 584). Dextrobromocamphorsulphonic acid is a far more powerful acid than tartaric acid, and hence might be expected to yield better characterised and more easily isolated salts than the latter, with the further advantage that with a monobasic acid there is usually no tendency to form two classes of salts. Dextrobromocamphorsulphonic acid is conveniently prepared from the ammonium salt by conversion into the barium salt and careful precipitation of the solution by sulphuric acid. After filtration, the strength of the resulting solution is determined by titration.

Tetrahydropapaverine is boiled with rather more than the calculated quantity of dextrobromocamphorsulphonic acid dissolved in a large quantity of water. Ultimately the whole dissolves, and, on cooling, long needles of lævotetrahydropapaverine dextrobromocamphorsulphonate,—

$$C_{20}H_{25}NO_4,C_{10}H_{14}BrO\cdot SO_3H,$$

crystallise out. Further quantities of this salt are obtained, mixed with increasing quantities of the more soluble dextrotetrahydropapaverine dextrobromocamphorsulphonate, on concentrating the mother-liquors. The two salts are readily separated by crystallisation from boiling water.

Lævotetrahydropapaverine dextrobromocamphorsulphonate crystallises readily from water, in which it is sparingly soluble in the cold, in long, colourless, anhydrous needles, melting with decomposition at 295—298°; it is somewhat more soluble in absolute alcohol, but insoluble in most other organic solvents. In a 0·3 per cent absolute alcoholic solution, it has the specific rotation about $[\alpha]_D = -30°$.

Dextrotetrahydropapaverine dextrobromocamphorsulphonate separates from solution as a resin which could not be obtained crystalline; when purified by repeated separation from its boiling aqueous solution and dried in the air, it forms a gritty, amorphous powder.

Lævotetrahydropapaverine, $C_{20}H_{25}NO_4$, separates on cooling a hot aqueous solution of its dextrobromocamphorsulphonate to which excess of ammonia has been added; it crystallises from boiling dilute alcohol in colourless, minute, six-sided plates containing water, which melt at 223°. The large flat face of the crystal is perpendicular to the acute bisectrix of a very small axial angle and of negative double refraction; the material has the specific rotation $[\alpha]_D = -149·5°$ in a chloroform solution containing 0·7987 grm. per 25 c.c. The *dextrotetrahydropapaverine* separated from its dextrobromocamphorsulphonate resembles the lævo-isomeride in all respects, but is of opposite rotation.

Inactive tetrahydropapaverine melts at 200—201°, and and at ordinary temperatures is crystallographically different from its optically active components; it is therefore a racemic compound in the sense of Kipping and Pope's definition (*Trans.*, 1897, lxxi., 989). It is formed on crystallising a mixture of equal weights of the two optically active isomerides from dilute alcohol.

The salts of racemic, dextro- and lævo-tetrahydropapaverine are being investigated, and experiments on other optically inactive alkaloids and their reduction products are in progress.

75. "*Molecular Weights of Permanganates, Perchlorates, and Periodates in Solution.* By J. Murray Crofts, B.A., B.Sc.

The molecular weight of potassium permanganate in solution has been determined only by the specific conductivity method. In view of the close relationship between manganese and chlorine indicated by the periodic classification of the elements, it was thought that further investigation of the molecular weights of these substances in solution would be of interest.

The method adopted was that devised by Löwenherz (*Zeit. Physik. Chem.*, 1895, xviii., 70), in which Glauber's salt is the solvent employed. In this solvent sodium salts cannot undergo dissociation. The methods by which practically pure crystalline sodium permanganate and the very deliquescent sodium perchlorate were obtained are described. Determinations with both the sodium and the potassium salts of the acids were made, and the results point to the formula $M'MnO_4$ for permanganates, and $M'ClO_4$ for perchlorates. For periodates (metaperiodates) the potassium salt only was used, and the constant obtained indicated KIO_4 as the formula.

The results afford additional evidence for the inclusion of manganese with the halogens in Group VII. of the periodic classification. The author is inclined to advocate Spring's formula for perchloric acid (*Bull. Acad. Belg.* [ii.], xxxix., 887), and a corresponding expression for permanganic acid, the chlorine and manganese atoms being regarded as heptavalent in these compounds.

76. "*The Action of Chlorine on Pyridine.*" By W. J. Sell, M.A., F.I.C., and F. W. Dootson, M.A.

In this communication the results are given of a repetition, in part, of the work of Keiser (*Am. Chem. J.*, 1886, viii., 308), undertaken primarily with the object of comparing his dichloropyridine hydrochloride with the trichloropyridine, melting at 71—72°, obtained by the authors by the action of phosphorus pentachloride on pyridine (*Proc.*, 1898, xiv., 110).

In consequence of the results obtained, the work was somewhat extended, and it is shown that (1) an additive compound of chlorine and pyridine is formed, the constitution of which is not yet established; (2) Keiser's dichloropyridine hydrochloride is a trichloropyridine; (3) others of the chloropyridines seem to be formed in small amount; (4) the compound, C_5H_5NCl, described by Keiser as an addition product of chlorine and pyridine, is pyridine hydrochloride.

77. "*The Oxidation of Paranitrotoluenesulphonic Acid to Dinitrostilbenedisulphonic Acid and to Paranitrobenzaldehydorthosulphonic Acid.*" By R. Herz and W. H. Bentley.

In this paper the authors describe their experiments on the oxidation of sodium paranitrotoluenessulphonate by sodium hypochlorite. By using much less caustic soda than Green and Wahl (*Ber.*, 1897, xxx., 3097), they find that the product of oxidation is almost entirely sodium dinitrostilbenedisulphonate, and that sodium dinitrodibenzyldisulphonate does not appear to be produced. The sodium, silver, barium, and lead salts, as well as the acid, have been prepared and examined.

The authors are unable to accept the views of Ris and Simon (*Ber.*, 1898, xxxi., 354) on the constitution of the stilbene derivative, and, from a determination of the amount of potassium permanganate required for its oxidation, maintain that it is a dinitro- and not a nitroso-nitro-compound. They found, independently of Green and Wahl, that, on oxidising sodium dinitrostilbenedisulphonate in the cold with potassium permanganate, sodium paranitrobenzaldehydorthosulphonate is formed. This substance possesses the properties of an aldehyde, and forms yellow crystalline compounds with phenylhydrazine and semicarbazide.

78. "*Determination of Molecular Weights: Modification of Landsberger's Boiling-point Method.*" By James Walker and John S. Lumsden.

The authors propose a modification of Landsberger's method (*Ber.*, 1898, xxxi., 458), which consists essentially in measuring the volume of the solution after the boiling-point has been determined, instead of ascertaining its weight. This is effected by graduating the boiling tube, and permits of a number of successive experiments being made with the same quantity of substance. Only one weighing is necessary for the whole series, which occasions a considerable saving of time, making it possible to obtain four or five determinations in the course of half an hour. The accuracy is comparable with that of the Victor Meyer vapour density method in ordinary circumstances.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 4.

On certain Molecular Changes between Soluble Salts capable of giving other Soluble Salts in a State of Purity. Conditions necessary; Applications.—E. Roca.—Not suitable for abstraction.

A Reaction of Aldehyds and Acetones.—MM. Lumière and Seyewitz.—If into a solution of 1000 grms. of water, 50 grms. of anhydrous sulphite of soda, and 10 grms. of pyrogallic acid we plunge a bromo-gelatin photographic plate which has had a normal exposure, it will be a long time, varying with the alkalinity of the sulphite and the sensibility of the plate, before an image appears; if, however, to the above solution we add successively various solutions of aldehyds or acetones, they will all considerably decrease the time which elapses before the image appears. The experiments were in every case made with 50 c.c. of the pyrogallic solution, and to this was added 1 grm. of either aldehyd or acetone dissolved in 25 c.c. of water or in 25 c.c. of alcohol when the compound was insoluble in water. A list of various aldehyds and acetones which have been tried is then given. The process can also be used for testing for certain compounds, and by its means, with the proper precautions, 1/25,000th part of methanal, 1/15,000th part of ethanal, and 1/2500th part of propanone have been detected.

Application of the Method of Friedel and Crafts for the Preparation of Aromatic Acetones and Aldehyds in vacuo. Reply to M. Bouveault.—A. Verley.—A controversial paper, not suitable for abstraction.

Action of Chloride of Acetyl on Acetate of Phenyl in the presence of Chloride of Aluminium. Preparation of Para-acetate of Phenyl.—A. Verley.—To about 3 molecules of acetate of phenyl, 1 molecule of chloride of aluminium is introduced, taking care to prevent all rise of temperature. The apparatus is exhausted, and then, drop by drop, one molecule of chloride of acetyl is added; the temperature should not exceed 20°. When no more HCl gas comes off, the contents are precipitated by water, and a substance boiling at 160° at 22 m.m. is distilled off. When crystallised from alcohol it appears under the form of brilliant white crystals and melts at 54°. By oxidation with dilute boiling nitric acid it is transformed into acetylparaoxybenzoic acid melting at 185°.

The Migration of the Atom of Iodine in the Nitration of Aromatic Derivatives. (III.).—F. Reverdin (in collaboration with K. Racer).—A long paper, not suitable for abstraction.

Action of Ethylic Aldehyd on Phenylhydrazin.—H. Causse.—The experiments here described show that ethanal acting on phenylhydrazin gives birth to two products. One is hydrazone, fusible at 99°, and is the first

formed; the second is triethylidenediphenylhydrazin, fusible at 109—110°.

Estimation of Oxygen Dissolved in Water.—MM. Albert Levy and F. Marboutin.—A reply to a criticism of a previous paper of theirs by M. Sokoloff in a Russian journal, the *Bparr*.

On the Essence of Basilic.—J. Dupont and M. Guerlain.—Under this name are included two products with very different properties, according to the place of their origin. That from France and Germany possesses a sweet characteristic odour; while that which comes from Reunion has, in addition, a strong odour of camphor, which nearly hides the other. Further, the first is levogyre and the second dextrogyre. After a number of other experiments, the authors are satisfied that chemically the essences from the plants cultivated in Europe are identical, while that from Reunion is from a different plant.

Journal de Pharmacie et de Chimie,
Series 6, vol. vii., No. 5.

The Estimation of the Phosphoglycerates.—MM. Adrian and Trillat.—The authors have verified the fact that glycerin does not intefere with the titration by means of indicators. For the estimation of phosphoric acid in the presence of glycerin, or of a neutral or acid phosphoglycerate or *vice versa*, an acid solution of phosphoglycerate of lime was prepared of such strength that 10 c.c. of the solution required 0·5 c.c. of potash to titrate it with heliantine, or 2·2 c.c. with phthalein. A mixture was made containing 10 c.c. of this solution, 10 c.c. of titrated phosphoric acid, and 10 c.c. of a solution of acid glycerophosphate and a few drops of glycerin. When titrated, this mixture required—With heliantine, 7·3 c.c.; with phthalein, 16·1 c.c. According to these figures, the sum of the acidities is divided in the following manner:—

	Heliantine.	Phthalein.
Acid glycerophosphate	0·5 c.c.	2·2 c.c.
Phosphoric acid	6·9 ,,	13·9 ,,
Total	7·4 ,,	16·1 ,,

Study of the Reaction of Phosphoric Acid on Glycerin.—MM. Adrian and Trillat.—The authors have endeavoured to prepare phosphoglyceric acid by Pelouze's method, and they obtained a product which on analysis partly corresponded to the acid phosphoglycerate of baryta. They also tried to decompose phosphoglycerate of potash by tartaric acid, as well as by other methods, but the result of their observation tends to show that there is not yet any known method of preparing phosphoglyceric acid in a state of purity; that this acid is decomposed by heat, and even by simple concentration, forming phosphoric acid; that the reaction of phosphoric acid on glycerin is complex, though limited; that there exists in conjunction with phosphoglyceric acid at least one diether, neutral to indicators, formed of one molecule of acid for two of glycerin, very slowly decomposable in the cold by the alkaline carbonates.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8. (Cantor Lectures). "Electric Traction," by Prof. Carus Wilson.

TUESDAY, 24th.—Royal Institution, 3. "The Historical Development of Modern Europe," by Samuel Rawson Gardiner, M.A., D.C.L., LL.D.

—— Society of Arts, 8. "The Goldfields of British Columbia," by W. Hamilton Merritt.

THURSDAY, 26th.—Royal Institution, 3. "Heat," by The Right Hon. Lord Rayleigh, F.R.S., &c.

FRIDAY, 27th.—Royal Institution, 9. "Sir Stamford Rafflea and the Malay States," by Lieut.-Gen. the Hon. Sir Andrew Clarke, R.E.

—— Physical, 5. "A simple Interference Method of Reducing Prismatic Spectra," by Messrs. Edser and Butler. "Some further Experiments on the Circulation of the Residual Gaseous Matter in Crookes Tubes," by Mr. Campbell Swinton.

SATURDAY, 28th.—Royal Institution, 3. "The Biology of Spring," by J. Arthur Thomson, M.A.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2009.

FIFTH ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1897.*

By F. W. CLARKE.

During 1897 comparatively few new determinations of atomic weights have appeared. The data given are as follows:—

Carbon.

Scott (*Journ. Chem. Soc.*, lxxi., 550, May, 1897) has carefully studied the determinations of the atomic weight of carbon which depend upon the combustion of the element and the weight of the dioxide formed, and has discovered an important correction. This is due to the considerable change of volume in the potash solution produced by the absorption of carbon dioxide, which involves a notable change in the reduction of the weighings to a vacuum. Scott has measured the amount of this change, and has applied it to the work of his predecessors with the subjoined results. In each case the values given are the means of the several experiments recorded.

	Uncorrected.	Corrected.
Dumas and Stas	11·9975	11·9938
Erdmann and Marchand.	12·0093	12·0054
Roscoe	12·0029	11·9973
Friedel	12·0112	12·0056
Van der Plaats.	12·0031	12·0018
Mean.. ..	12·0048	12·0008

These values are based upon O=16; with O=15·879, the corrected mean result becomes C=11·910.

Scott further criticises in detail the determinations by Stas which depend upon the combustion of carbon monoxide, and shows that they require possible corrections and involve various uncertainties. He concludes "that the atomic weight of carbon is by no means one of those most accurately known, and that a careful revision of it is imperative."

Nitrogen, Chlorine, and Silver.

Leduc (*Comptes Rendus*, cxxv., 299, August 2, 1897), on the basis of his density determinations, assumes N=14·005 when O=16. Applying this to the determinations by Stas of the ratios Ag:Cl, AgCl:O_3, and AgCl:NH_4Cl, he finds a discrepancy of about 1 part in 320. That is, the work of Stas gives N=14·044 instead of 14·005. This disagreement Leduc attributes to the presence of occluded oxygen, as pointed out by Dumas, in the silver used by Stas. For this he assumes a correction, and then, combining his value for nitrogen with the data given by Stas, he computes H=1·0076, Cl=35·470, and Ag=107·916. The correction applied by Leduc seems to be somewhat uncertain; and it is doubtful whether his determination of the density of nitrogen is entitled to greater weight than the other data which are involved in the calculations.

Aluminum.

In the third and fourth reports of this committee, Thomsen's data for the atomic weight of oxygen are given. In these determinations oxygen and hydrogen were compared with aluminum as an intermediary; but the aluminum used was not absolutely pure. Had it been pure, the atomic weight of the metal, with reference to the two gases, could have been computed.

Thomsen now (*Zeit. Anorg. Chem.*, xv., 447) gives the data necessary for the comparison, and deduces the atomic weight of aluminum. The impurities are determined and corrections for them applied. There is also a correction for the change in volume of the potash solution in which the metal was dissolved. Applying the corrections, Thomsen finds that 0·99897 grm. pure aluminum correspond to 0·11195 grm. of hydrogen. Hence, with H=1,—

Al = 26·770.

Again, 0·99897 grm. of metal is equivalent to 0·88824 grm. of oxygen. Hence, with O=16,—

Al = 26·992.

These two values, referring to the two standard units, are determined independently of each other, and are independent of any measured ratio between O and H. They are notably lower than the values computed by myself from Mallet's data, 26·91 and 27·11, and possibly should supplant the latter. This question, however, needs further discussion, and probably some additional experiments.

Nickel.

Atomic weight determined by Richards and Cushman (*Proc. Amer. Acad.*, xxxiii., 97, November, 1897), from analyses of the anhydrous sublimed bromide, $NiBr_2$. This substance is shown by the authors to be perfectly suited to the purpose of the investigation. The method of analysis was in all essential respects that used by Richards in other researches of the same kind, and was partly gravimetric and partly volumetric. On the one hand, the ratio $2AgBr : NiBr_2$ was determined; on the other, the ratio $2Ag : NiBr_2$. All weighings were reduced to a vacuum. The results, in three series, were as follows:—

First Series.

Weight $NiBr_2$.	Weight AgBr.	Atomic weight Ni.
2·26113	3·88769	58·646
2·80668	4·82431	58·708
1·41317	2·42880	58·716
1·71759	2·95307	58·650
2·48565	4·27357	58·651
4·32997	7·44280	58·700
2·18072	3·74856	58·693
	Mean.. ..	58·680

Second Series.

Weight $NiBr_2$.	Weight AgBr.	Atomic weight Ni.
3·28039	5·63892	58·691
2·70044	4·64208	58·686
3·38230	5·81391	58 698
1·33459	2·29435	58·670
1·25054	2·14963	58·693
1·32778	2·27384	58·690
2·24452	3·85805	58·705
	Mean.. ..	58·690

Third Series.

Weight $NiBr_2$.	Weight Ag.	Atomic weight Ni.
3·28039	3·23910	58·701
2·70044	2·66636	58·709
3·38230	2·33990	58·689
1·33459	1·31787	58·689
1·25054	1·23482	58·698
1·32278	1·30629	58·675
2·24452	2·21652	58·676
	Mean.. ..	58·691

From all these data the authors conclude that the atomic weight of nickel cannot be far from 58·69, when O=16, or 58·25 if O=15·88.

* From the *Journal of the American Chemical Society*, xx., No. 3.

From series two and three 15·32086 grms. of silver give 26·67078 grms. of bromide. Hence the percentage of silver in silver bromide is 57·444, which agrees with the value 57·445 found by Stas. This is a good check upon the accuracy of the work.

Cobalt.

The atomic weight determinations by Richards and Baxter (*Proc. Amer. Acad.*, xxxiii., 115, December, 1897) are in all essential respects like those of nickel which have just been cited. The three series of data are as follows:—

First Series.

Weight $CoBr_2$.	Weight AgBr.	Atomic weight Co.
2·25295	3·86818	58·950
2·88763	4·95732	58·957
1·88806	3·24056	59·026
	Mean.. ..	58·984

Second Series.

Weight $CoBr_2$.	Weight AgBr.	Atomic weight Co.
1·33564	2·29296	58·975
2·58129	4·43095	58·998
2·84382	4·88135	59·009
1·83722	3·15368	59·000
2·68584	4·61046	58·996
3·18990	5·47607	58·982
2·88914	4·95943	58·997
2·32840	3·99706	58·987
1·91703	3·29053	59·010
	Mean.. ..	58·995

Third Series.

Weight $CoBr_2$.	Weight Ag.	Atomic weight Co.
1·33564	1·31702	59·002
2·58129	2·54585	58·955
2·84382	2·80449	58·977
1·83722	1·81170	58·991
2·68584	2·64879	58·969
2·88914	2·84891	58·998
2·32840	2·29593	59·003
1·91703	1·89033	58·999
	Mean.. ..	58·987

If O=16, Co=58·99, as the outcome of all the series. If O=15·88, Co=58·55. From the data in series two and three the percentage of silver in silver bromide is 57·446, while Stas gives 57·445. The last five experiments, which are the best, give 57·447. This check on the accuracy of the work is therefore satisfactory.

Tungsten.

The investigation by Hardin (*Journ. Am. Chem. Soc.*, xix., 657, August, 1897) is rather the scrutiny of a method than an attempt to accurately fix an atomic weight. Most of the determinations of the atomic weight of tungsten have been based upon analyses or syntheses of the trioxide; and this substance is now shown to be exceedingly untrustworthy as regards the measurement of this constant. Hardin has made sixty-four determinations with the trioxide, in seventeen groups or series, using material from various sources, and working under a great variety of conditions. The values found range from W=183·51 to W=185·00 when O=16; the average of all being 184·106. The same discordance appears upon comparing the results obtained by previous investigators, and it seems to be partly due to absorptions of tungsten or its oxide by the boat in which the reductions or oxidations were effected, and partly to the presence of nitrogen in the trioxide when the latter was prepared from ammonium tungstate. At all events, the method is unsuited to its purpose, and the atomic weight of tungsten needs thorough re-investigation by means of other processes.

Cerium.

The atomic weight of this metal has been re-determined by Wyrouboff and Verneuil (*Bull. Soc. Chim.*, [3], xvii., 679) upon material purified by an elaborate process and with extreme care. From this material the oxide CeO_2 was obtained perfectly white—a result in corroboration of the researches of Wolf and of Wing, but contrary to later investigators who have always found the substance to be more or less coloured. The existence of a white oxide is also confirmed by the recent investigations of Moissan (*Comptes Rendus*, cxxiv., 1233).

The salt chosen for the atomic weight determinations was the sulphate, $Ce_2(SO_4)_3.8Aq$, a compound which is perfectly definite and stable, and which is easily obtained in a state of purity. At 250° it loses its water with facility, and up to 500° it undergoes no further decomposition. By ignition at a white heat, 1500° approximately, all sulphuric acid is expelled, and the pure oxide remains. The other hydrated sulphates of cerium are less manageable. The material studied was derived from three distinct sources, partly from monazite, partly from cerite; and the results obtained confirm one another. The weights were as follows, but nothing is said as to their reduction to a vacuum. Probably the reduction was not made:—

First Sample.

Hydrous salt.	Anhydrous salt.	CeO_2.
1·2385	0·9875	0·5977
1·2730	1·0148	0·6138
1·2030	0·9590	0·5794
1·5420	1·2295	0·7430

Second Sample.

0·9642	0·7685	0·4642
1·3260	1·0571	0·6389
1·1429	0·9112	0·5518
0·9072	0·7232	0·4372

Third Sample.

1·2114	0·9658	0·5840
1·2411	0·9894	0·5984

From these data the following atomic weights are derived when O=16 and S=32, cerium being regarded by the authors as a dyad, with the oxide obtained having the formula Ce_3O_4.

First Series.

	From per cent H_2O.	From "Ce_2O_4" in hydrate.	From Ce_3O_4 in anhydrous salt.
	92·84	93·08	93·16
	92·65	92·88	92·95
	92·65	92·64	92·63
	92·85	92·74	92·70
Mean ..	92·74	92·84	92·86

Second Series.

	92·49	92·55	92·56
	92·69	92·72	92·73
	92·76	93·17	93·30
	92·66	92·77	92·80
Mean ..	92·65	92·80	92·85

Third Series.

	92·75	92·84	92·87
	92·68	92·88	92·93
Mean ..	92·71	92·86	92·90
Mean of all	92·70	92·83	92·87

The extreme variation is 0·75, which becomes 1·125 when cerium is regarded as a triad.

From the entire series of determinations, the salt $Ce_2(SO_4)_3.8Aq$ gives in mean 20·278 per cent of water, and 48·205 CeO_2. The mean percentage of CeO_2 in the anhydrous sulphate is 60·467. From these data, with H=1, O=15·879, and S=31·83, the following mean values for Ce''' are deduced:—

From percentage of water .. .. Ce=138·14
From CeO_2 in hydrated salt .. .. Ce=138·35
From CeO_2 in $Ce_2(SO_4)_3$ . .. .. Ce=138·42

The mean of these is Ce=138·30. With O=16, this becomes Ce=139·35.

These figures are adopted in the table at the close of this report, as being probably more trustworthy than the older determinations, but they are still subject to a good deal of uncertainty.

Still another investigation upon cerium is reported by Boudouard (*Comptes Rendus*, cxxv., 772), who, following Schützenberger, fractionates the salts of the metal. His atomic weight determinations are made by ignition of the sulphate; but the values assigned to O and S are not stated. By fractionation of the acetate he gets an oxide giving from Ce=135·1 to 140·7. From fractionations of the sulphate he finds Ce=133·0 to 138·75. Hydrogen peroxide precipitates an oxide giving Ce=137·15 to 137·6, while the unprecipitated portion ranges from 137·85 to 139·9. He concludes that the oxide of cerium is accompanied by small quantities of another earth of lower atomic weight.

Wyrouboff and Verneuil (*Comptes Rendus*, cxxv., 950) criticise the work of Boudouard, and suggest that his high values for Ce are due to the presence of thoria, while the lower values are ascribable to the other earths of the cerium-yttrium groups. To this criticism Boudouard replies (*Comptes Rendus*, cxxv., 1096), defending the purity of his material. He now states that his CeO_2 was *white*. Wyrouboff and Verneuil (*Comptes Rendus*, cxxv., 1180) reiterate their objections, and show that the variations in successive portions obtained by Boudouard are irregular, sometimes high, sometimes low, and not systematic in one direction as they should be with material representing an orderly fractionation.

It is evident from the discussion thus summarised that Boudouard's figures relate to mixtures, and not to one earth, whatever the mixtures may be. They are therefore unavailable as determinations of a definite atomic weight. It may be suggested here that a careful scrutiny of the supposed CeO_2 is necessary in order to prove that it is not contaminated by higher or lower oxides of cerium, and that it does not contain, like certain other oxides, occluded gaseous impurities. Until these questions have been settled, all atomic determinations based upon weighings of ceric oxide are uncertain.

Gaseous Densities.

Lord Rayleigh (*Nature*, December 30, 1897; CHEMICAL NEWS, December 31) has continued his investigation upon the density of the principal gases, and now gives data for CO, CO_2, and N_2O. His results, air being taken as unity, are tabulated as follows:—

Oxygen	1·10535
Atmospheric nitrogen, plus argon.	0·97209
Nitrogen	0·96737
Argon	1·37752
Carbonic oxide	0·96716
Carbon dioxide	1·52909
Nitrous oxide	1·52951

Calculated from the density of Co, with O=16, C=11·9989.

Mathematical Relations.

Rummel (*Proc. Roy. Soc. of Victoria* (Australia), x., Part 1, p. 75), in a paper upon "The Spectra of the Alkalis and their Atomic Weights," works out a series of

	H = 1.	O = 16.
Aluminum..	26·91	27·11
Antimony	119·52	120·43
Argon..	?	?
Arsenic	74·44	75·01
Barium	136·39	137·43
Bismuth	206·54	208·11
Boron..	10·86	10·95
Bromine	79·34	79·95
Cadmium	111·10	111·95
Cæsium	131·89	132 89
Calcium	39·76	40·07
Carbon	11·91	12·00
Cerium	138·30	139·35
Chlorine	35·18	35·45
Chromium..	51·74	52·14
Cobalt..	58·55	58·99
Columbium	93·02	93·73
Copper	63·12	63·60
Erbium	165·06	166·32
Fluorine	18·91	19·06
Gadolinium	155·57	156·76
Gallium	69·38	69·91
Germanium	71·93	72·48
Glucinum	9·01	9·08
Gold	195·74	197·23
Helium	?	?
Hydrogen	1·000	1·008
Indium	112·99	113·85
Iodine	125·89	126·85
Iridium	191·66	193·12
Iron	55·60	56·02
Lanthanum	137·59	138·64
Lead	205·36	206·92
Lithium	6·97	7·03
Magnesium	24·10	24·28
Manganese	54·57	54·99
Mercury	198·49	200·00
Molybdenum	95·26	95·99
Neodymium	139·70	140·80
Nickel	58·24	58 69
Nitrogen	13·93	14·04
Osmium	189·55	190·99
Oxygen	15·88	16·00
Palladium	105·56	106·36
Phosphorus	30 79	31·02
Platinum	193·41	194·89
Potassium..	38·82	39·11
Praseodymium.. ..	142·50	143·60
Rhodium	102·23	103·01
Rubidium	84·78	85·43
Ruthenium	100·91	101·68
Samarium	149·13	150·26
Scandium	43·78	44·12
Selenium	78·42	79·02
Silicon	28·18	28·40
Silver..	107·11	107·92
Sodium	22·88	23·05
Strontium	86·95	87·61
Sulphur	31·83	32·07
Tantalum	181·45	182·84
Tellurium	126·52	127·49
Terbium	158·80	160·00
Thallium	202·61	204·15
Thorium	230·87	232·63
Thulium	169·40	170·70
Tin	118·15	119·05
Titanium	47·79	48·15
Tungsten	183·43	184·83
Uranium	237·77	239·59
Vanadium	50·99	51·38
Ytterbium	171·88	173·19
Yttrium	88·35	89·02
Zinc	64·91	65·41
Zirconium..	89·72	90·40

relations which seem to be significant. For the formulæ developed, which are algebraic, the original paper must be consulted. When Na=23, as the starting-point, the spectral relations give He=3·64, K=39·05, Rb=85·15, and Cs=133·47. These values are near enough to the actual determinations to show that the mathematical process deserves careful consideration.

Miscellaneous Notes.

At the Toronto Meeting of the British Association for the Advancement of Science, Brauner presented a paper on the atomic weight of thorium. Also at the Washington Meeting of the American Chemical Society, Venable gave the preliminary results of an investigation upon zirconium (see CHEMICAL NEWS, vol. lxxvii., p. 221).

A memoir upon the atomic weight of molybdenum by A. Vandenberghe, has been awarded the Stas prize of the Belgian Academy. It will appear in the quarto form adopted by the Academy for its more important publications.

The accompanying table of atomic weights is essentially that given in Clarke's "Re-calculation," a new edition of which was published by the Smithsonian Institution in January. The names of elements which represent changes from the table of 1896 are italicised.

GLADDING'S METHOD FOR PHOSPHORIC ACID.

By JOHN B. COPPOCK, F.C.S.,
Lecturer, Lancashire County Council Agricultural School.

IN the CHEMICAL NEWS (vol. lxxvii., p. 32) Gladding gives a method for the gravimetric estimation of phosphoric acid as ammonium phosphomolybdate, which can be applied to fertilisers.

Although generally attempts to estimate the amount of phosphoric acid by precipitation and weighing as the yellow ammonium phospho-molybdate have not given reliable results, there seems to be no reason why Gladding's method should not be widely applied for phosphoric acid determination in fertilisers.

In some analyses which have recently passed through my hands, I have made comparisons between the magnesia method and the Gladding method. The point in favour of the Gladding method is the quickness of the determination.

The following results have been obtained:—

Boiled Bones.

	Magnesia method.	Gladding's method.
Sample I.	25·22	25·80
„ II.	23·18	23·85

In each case the figures represent the percentage of phosphoric acid present. Correcting the figures in the magnesia method by adding 0·33 (the usual solubility allowance) we get—

25·55 per cent phosphoric acid
23·51 „ „ „

which shows that the new method is quite satisfactory for fertiliser work.

Superphosphates.

Superphosphates gave the following figures in two cases:—

	Magnesia method.	Gladding's method.
Sample I.	16·34	16·50
„ II.	15·17	15·32

Thus, although the figures are invariably higher for Gladding's method, they are exact enough for fertiliser work. If the method is used the nitric acid can be added at once to the extent of 50 c.c. if the acid is of specific gravity 1·42 and the ammonia of specific gravity 0·88. The solution is then quite acid enough for the precipitation of the yellow salt by the addition of 40 c.c. of the usual 5 per cent molybdic oxide solution. This is quite sufficient acid solution to ensure complete precipitation if 0·25 grm. of the fertiliser has been used.

My precipitates were dried first in the water-bath, then finished in the air-bath, despite the fact that the author of the method discarded his air-bath for a glycerol one.

Washing the precipitate off smoothened filter-paper into a platinum dish was tried, as in the determination of phosphoric acid in basic slag as ammonium phosphomolybdate. The results are quite satisfactory. There can be no doubt that the method affords a quick and reliable way for the determination of phosphoric acid in fertilisers.

THE PREPARATION OF CARBONATE OF MENTHOL.

By M. ERDMANN.

MENTHOL appears to have been used medicinally with some success during the past few years; but its use is often limited by the caustic action it has on the mucous membrane, so that some writers have proposed substituting carbonate of menthol instead.

This product has been described by G. Arth (*Ann. de Chim. et de Phys.*, 1886, vii., 469), who obtained it by the action of cyanogen gas or of chloride of cyanogen on sodium-menthol. The principal product of this reaction is menthylurethane, and carbonate of menthol only occurs as a by-product in small quantities.

The pyridine method, used to effect substitutions to the functional hydrogen of the terpenic alcohols, gives a rapid and convenient method of preparing carbonate of menthol. The method of operating is as follows. To a solution of—

Menthol	30 grms.
Chloroform	30 c.c.
Pyridine (anhydrous) ..	25 „

we add, by small portions, a chloroformic solution of phosgene containing 10 grms. of $COCl_2$, stirring the whole time. This is then left to stand for twenty-four hours, then, without separating the two layers of liquid, it is treated by steam. Traces of uncombined menthol pass off at the same time as the pyridine. The residue consists of crystalline carbonate of menthol, which is washed with warm water and re-crystallised in a large quantity of warm alcohol. The carbonate, hardly soluble in alcohol in the cold, is deposited in long white prisms melting at 105° precisely. The reaction is almost quantitative.—*Journ. für Prakt. Chemie*, lvi., p. 43.

ON THE ESTIMATION OF MANGANESE SEPARATED AS THE CARBONATE.*

By MARTHA AUSTIN.

THE estimation of manganese precipitated as the manganous carbonate, when that salt is obtained by the action of sodium or potassium carbonate, has been regarded as very undesirable for the reasons that, even if the conditions of the precipitate is such that it does not run through the filter, the manganous carbonate can never be freed entirely from alkaline salt, and that the conversion of the carbonate to the manganosomanganic oxide—the form in which it is customary to weigh—is too uncertain. It had been supposed also that the presence of ammoniacal salts (as well as of carbonic acid) causes solution of the

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. v., p. 382.

Table I.

$MnCl_2$. C.m.s.	MH_4Cl. Grms.	$MnCO_3$. Found.	$MnCO_3$. Theory.	$MnCO_3$. Error.	Mn_3O_4. Found.	Mn_3O_4. Theory.	Mn_3O_4. Error.
50	10	0·2685	0·2680	0·0005+	0·1770	0·1776	0·0006−
50	10	0·2704		0·0024+	0·1788		0·0012+
50	10	0·2710		0·0030+	0·1770		0·0006−
50	10	0·2720		0·0040+	0·1774		0·0002−

Table II.

	MH_4Cl. Grm.	Mn_3O_4. Found.	Mn_3O_4. Theory.	Mn_3O_4. Error.	$MnSO_4$. Found.	$MnSO_4$. Theory.	$MnSO_4$. Error.
1.	10	0·2463	0·2478	0·0015−	0·4903	0·4905	0·0002−
2.	10	0·1110	0·1121	0·0011−	0·2225	0·2219	0·0006+
3.	10	0·1584	0·1581	0·0003+	0·3126	0·3128	0·0002−
4.	10	0·1672	0·1699	0·0027−	0·3355	0·3364	0·0009−

manganous carbonate, until the work of Guyard (Hugo Tamm) (Chemical News, xxvi., 37) showed that when the precipitation is accomplished by ammonium carbonate, even in the presence of ammonium chloride, complete separation of the manganese is possible. No data are given by Guyard to show the completeness of the separation of the manganese by this process; but Fresenius (*Zeit. f. Anal. Chemie*, 1872, 290) examined the method and speaks favourably of it. In this process the main difficulty of the older method of estimation of the carbonate—viz., the inclusion of the alkaline salt—is avoided. We know now how to avoid the difficulty in the way of weighing as the oxide by converting that substance to the form of the sulphate, as shown in a former paper (*Am. Journ. Sci.*, IV., v., 209).

For a careful study of the separation of manganous carbonate by Guyard's method a solution of pure manganous chloride was prepared and standardised as the anhydrous sulphate in the manner detailed in the paper to which reference has been made above. A definite volume of the manganous chloride was carefully drawn into a platinum dish and diluted to a volume of 200 c.c. To the solution heated to 100° C. ammonium chloride (about 10 grms.) was added and ammonium carbonate in excess. The solution was kept warm until the precipitate subsided, and then was filtered off on asbestos on a perforated crucible under pressure. The presence of ammonium chloride is necessary to insure such a condition of the precipitate that it will not run through the felt.

Inasmuch as the precipitate was collected under conditions which readily permit an attempt to weigh as the carbonate, a trial of that method was made incidentally. The event proved as Rose (*Ann. Phys. Chem.*, 1851, lxxxiv., 52) has stated previously, that when the carbonate is gently heated, evolution of carbon dioxide and oxidation of the residue begins before the water is thoroughly removed; for, though nearly all the results are above the theory, the solution of the residue in hydrochloric acid indicated plainly the presence of a small amount of a higher oxide of manganese. In Table I. are found the results of a series of experiments in which the attempt was made to weigh first as carbonate and again after strong ignition—well within the oxidising flame of a powerful burner (*Am. Journ. Sci.*, IV., v., 209)—as the manganoso-manganic oxide. The application of the bromine test to the hot ammoniacal filtrate showed that, in every one of these experiments, the precipitation of the manganese in the form of the carbonate had been complete.

As shown in Table I., weighing as the carbonate is out of the question; the errors of the process when the residue is ignited in the manner described to form the manganoso-manganic oxide are much smaller, though rather variable. The estimation of manganese as the anhydrous sulphate had given, in the work to which reference has been made, results agreeing so much more closely than could be obtained by any other method of procedure, that the attempt was made to estimate the amount of manganese precipitated as the manganese carbonate by converting it first to the oxide, then to the sulphate. A given weight of sulphate was precipitated as the manganous carbonate, after the employment of all the precautions mentioned previously in this paper, and then filtered off on ashless filter-paper. After washing thoroughly with hot water, the filter was burned, the residue ignited for the condition of the manganoso-manganic oxide and weighed as such. Then the oxide was converted to the sulphate by heating with three or four drops of concentrated sulphuric acid. The agreement of the results, as shown in Table II., is considerably better.

By treatment of the filtrates of 1, 2, and 3 with bromine and ammonia at boiling temperature, no manganese was found. In the filtrate from No. 4, by the same treatment, a small amount of manganese dioxide was precipitated, which, when heated with concentrated sulphuric acid, gave 0·0006 grm. of manganous sulphate; and, hence, the error in that determination is really 0·0003 grm. on the sulphate. The slightly larger deficiency recorded in the table was probably due to imperfect filtering.

It seems to be evident that Guyard's method of separation of manganese as the manganous carbonate, when handled with precautions, gives complete separation of that element. It must be recognised clearly, however, that the precipitation should be made in the presence of a considerable amount of ammonium chloride, and that great care must be used in the filtering and washing of the finely divided precipitate. It is altogether preferable to weigh in the condition of the sulphate.

In conclusion thanks are hereby expressed to Professor F. A Gooch for kind assistance.

THE DISSOCIATION OF ELECTROLYTES AS MEASURED BY THE BOILING-POINT METHOD.*

By HARRY C. JONES and STEPHEN H: KING.

The two methods of general application for measuring the amount of electrolytic dissociation in aqueous solutions, are, the conductivity method of Kohlrausch (*Ann. der Phys., Wied.*, xxvi., 161), and the freezing-point method of Beckmann in its most improved forms (*Ibid.*, li., 500; *Zeit. Phys. Chem.*, xi., 529). There are, in addition, several methods available for determining the concentration of particular kinds of ions, or which admit of application to a limited number of cases, as the well-known solubility method of Nernst and Noyes (*Zeit. Phys. Chem.*, iv., 372; vi., 241). The two methods, which can be used satisfactorily with water solutions, are, in turn, of limited applicability when other solvents are employed. The use of conductivity as a direct measure of dissociation is most satisfactory when water is used

* From the *American Chemical Journal*, vol. xix., No. 9.

as a solvent. A difficulty which is encountered with other solvents is, that the dissociation in them is not complete at dilutions which come within the range of that method. The value of $M\infty$ cannot, therefore, be determined directly, and some assumption, which may require proof, is sometimes made in an attempt to determine its approximate value. Considerable work has, however, already been done on the conductivity of solutions of electrolytes of different concentrations in solvents other than water, —notably the work of Fitzpatrick (*Phil. Mag.*, 377, 1887), Paschkow ("Uber die Leitfähigkeit einiger Salze in Alkohol Lösungen," Charkow, 1892), and Völlmer (*Ann. der Phys., Wied.*, lii., 328), on solutions in ethyl and methyl alcohol; of Zelinsky and Krapiwin (*Zeit. Phys. Chem.*, xxi., 35), on solutions in methyl alcohol; and of Zanninovich-Tessarin (*Ibid.*, xix., 251), on solutions in formic acid.

The freezing-point method can also be successfully applied to only a limited number of solvents, and especially well only to water solutions. It may, perhaps, be applicable to solutions in benzene, acetic acid, and other solvents whose freezing-points are not widely removed from the ordinary temperature. But many solvents do not come within its range because their points of solidification lie too low to enable one to apply the freezing-point method with even a fair degree of accuracy. For such solvents it seems that the boiling-point method is the only one available, and this only when it has been worked out with sufficient accuracy to enable one to place a fair amount of confidence in the results. On the other hand, the boiling-point method is not easily applied to water solutions, owing in part to the very small value of the constant for that solvent.

One of the causes why the physical chemistry of to-day is primarily the physical chemistry of water solutions, is doubtless the greater dissociating action of that solvent. But another, which is strongly operative, is the absence of a reliable method with which to measure accurately the amount of dissociation in other solvents. This alone would show the importance attached to such determinations.

The interest in such measurements is, however, still further increased by the relation between the dielectric constants of solvents and their dissociating power, which has been pointed out on theoretical grounds for the first time in a readily accessible scientific journal, by J. J. Thomson (*Phil. Mag.*, xxxvi., 320), and about the same time by W. Nernst (*Göttinger Nachrichten*, 1893, and *Zeit. Phys. Chem.*, xiii., 531). Whether such a relation exists rigidly and quantitatively, whether dissociating power is a function of any one physical property of the solvent, can be determined only by a careful study of the dissociation of electrolytes in the different solvents in question. In order that such work may be done, it is necessary that a method be worked out which will meet the requirements of practicability and accuracy.

The object of this preliminary notice is to call attention to the fact that we have such, in an improved form of the Beckmann boiling-point method, which he devised for the determination of the molecular weights of non-electrolytes. The essential feature in the new boiling-point apparatus (*Amer. Chem. Journ.*, xix., 581) is the introduction of a platinum cylinder around the thermometer, which cuts off the effect of radiation, and at the same time prevents the condensed solvent from coming in contact with the thermometer until it has been re-heated. The determinations of the molecular weights of a number of non-electrolytes in five solvents, whose boiling-points vary from 35° to 182°, show that we have to deal with the simplest efficient boiling-point apparatus thus far constructed. We have already applied it to the measurement of the electrolytic dissociation of solutions of two electrolytes, potassium iodide and sodium acetate, in ethyl alcohol, and the results will show the degree of accuracy of which the method is capable.

The reason why the boiling-point method has not already found extensive application in measuring dissociation is, doubtless, to be sought in the fact that it has not been worked out with accuracy sufficient to enable it to be applied with a fair degree of probability.

The alcohol used in this work was dehydrated in the usual manner. It was allowed to stand for some days over quicklime, distilled and preserved in contact with anhydrous copper sulphate. The sodium acetate used was prepared by dissolving metallic sodium in water, neutralising the sodium hydroxide formed with acetic acid, evaporating the solution of sodium acetate to dryness, and finally drying in an air-bath, above 100°, to constant weight. The results given below are distinctly tentative, and solutions of both of the compounds in question will be worked over in the future with still greater care than has been possible thus far. The prime object in publishing these values at present is to show the fair agreement between the dissociation values as determined for the same substances, under the same conditions.

The Results.

Solvent, Alcohol. Molecular rise in 100 grms., 11·5°.

Potassium Iodide, molecular weight 166.

Grms. solvent.	Grms. potassium iodide.	Grms. iodide to 100 grms. solvent.	Rise in boiling-point.	Molecular rise.	Dissociation. Per cent.
53·553	1·6470	3·076	0·271°	14·625	27·2
56·234	1·2945	2·302	0·200	14·419	25·4
54·533	1·080	1·9804	0·172	14·417	25·4
58·572	1·389	2·371	0·208	14·566	26·7
58·900	1·060	1·800	0·158	14·576	26·7

Sodium Acetate, molecular weight 82·1.

Grms. solvent.	Grms. sodium acetate.	Grms. acetate in 100 grms. solvent.	Rise in boiling-point.	Molecular rise.	Dissociation. Per cent.
57·599	0·747	1·2969	0·185°	11·711	1·8
57·599	1·217	2·1129	0·299	11·616	1·0
57·878	0·5997	1·0361	0·147	11·648	1·3
57·878	0·9715	1·6785	0·238	11·640	1·2

In these determinations the barometer was read every few minutes, and the boiling-points were corrected for any change in atmospheric pressure, however slight. While very small changes in the barometer can be neglected when the question under investigation is one of molecular weights, they must always be carefully taken into account when far more accurate measurements are necessary, as in the case of the measurement of dissociation.

It will be seen from the results that the dissociation of potassium iodide in alcohol is between one-third and one-fourth of that in water at the same dilution. This is just about the same ratio as exists between the dielectric constants of these two solvents.

The dissociation found for sodium acetate in alcohol is almost certainly too low. Indeed the metallic sodium used in preparing the hydroxide was found to contain more than a trace of potassium, and this may account in part for the very low values.

We propose to extend the application of this method to a large number of electrolytes, and to as many solvents as may be practicable.

A Reception was held on Tuesday, the 24th inst., at the Galleries of the Royal Institute of Painters in Water Colours, Piccadilly, by Dr. and Mrs. Stevenson, Prof. and Mrs. Frank Clowes, and Dr. and Mrs. Bernard Dyer, representing the Institute of Chemistry of Great Britain and Ireland, the Society of Chemical Industry, and the Society of Public Analysts. The reception was very well attended, and a good programme of music was given, interspersed with humorous glees.

ON THE

SEPARATION OF THE OXIDES OF CERIUM AND THORIUM.*

By G. WYROUBOFF and A. VERNEUIL.

Ever since the commencement of our researches on the rare earths we have been endeavouring to find more certain, and above all more rational, methods of separation than those which have been in use up to the present time. All the known processes are in fact empirical; they do not depend on any definite or precise reaction, and, moreover, do not lead to any result except by a long series of fractionations. Further, we can never be sure of the purity of the substance obtained, except by spectroscopic observations, in the case when the spectrum is very characteristic, or by the absence of incandescence when dealing with thorina. Nevertheless all these earths, closely allied as they are, ought to have characteristic reactions; it is only under such conditions that they can be considered as distinct chemical species. The problem is thus reduced to finding these characteristic reactions, and to make the best use of them.

Let us first remark that, in placing the rare earths according to their chemical analogies, we obtain the following series:—Th, Ce, La, D, Yt (Er, Te). This series presents one extremely interesting peculiarity. If we succeed by any special process in completely separating one term of the series from the term immediately following it, we separate it, at the same time, from all those terms which follow, and leave all which precede it. It is due to this that all the known methods for separating the yttria earths from didymium carry with the latter not only the other cerite earths, but also thorina; it is equally for this reason that the reactions which enable us to obtain cerium, free from lanthanum and didymium, eliminate at the same time the yttria earths, but necessarily carry down thorina. We shall later on give a very simple explanation of this apparently singular phenomenon; but for the present it suffices to make the fact known, as it should serve as a basis for all rational methods for the separation of the rare earths. We are doubtless still far from possessing methods of separation for all the metals of the series, but for some of them this is already possible, and we now propose to describe the conditions of the reactions.

In a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xvii., p. 679, 1897) we gave a very simple method for the complete separation of cerium from lanthanum and didymium. Conformably with the rule we have just laid down the yttria earths are eliminated at the same time, but also, conformably with this rule, the thorina remains with the cerium. It is necessary for us to obtain cerium rigorously free from lanthanum, didymium, and thorium; the problem is set in a very precise manner; the lanthanum and didymium, and the yttria earths, are all eliminated at the same time. We must now search for a reaction which will enable us to immediately separate the thorium. The solution of the problem stated in these terms does not present any difficulty. Phosphate of thorium is, in fact, quite insoluble in dilute hydrochloric acid; cerous phosphate is, on the other hand, easily soluble. If, therefore, to a mixture of chlorides containing a little thorina, we add enough phosphoric acid to saturate the latter, it separates integrally, carrying down with it, it is true, variable quantities (a few hundredths) of cerium. But in this form phosphate of thorium is an exceedingly voluminous body, very difficult to filter and wash. It is therefore necessary, after the addition of the phosphoric acid, to evaporate the whole, either on a water-bath or over a naked flame, to a pasty consistency; take up with HCl diluted with about seven or eight times its volume of water. The washing of the precipitate is then very easy, and the filtrate does not contain a trace of thorium. To prove the absence of thorium a reagent is necessary, capable of showing even very minute quantities, and this we have in peroxide of hydrogen. It is in this manner that we have succeeded in solving not only the inverse problem,—the easy preparation of thorium free from cerium,—but also in effecting the quantitative separation of the two bodies.

M. Clève noticed, a long time back (*Bull. Soc. Chim.*, xliii., p. 57, 1885), that on adding an excess of peroxide of hydrogen to a solution of sulphate of thorium, we obtain a voluminous white precipitate composed as follows:—$Th_4O_7SO_3$, (Th=116). This compound is not completely insoluble, and the filtrate gives a more or less abundant precipitate with ammonia. This is caused by the presence of free sulphuric acid which is formed during the reaction,—

$$4SO_4Th + 3H_2O_2 = Th_4O_7SO_3 + 3H_2SO_4,$$

and which tends to decompose the peroxide formed. It thus seemed probable that by using a less energetic acid we might succeed in completely precipitating the thorina, the more so as a similar reaction has long been known with cerium. We know, in fact, that acetate of cerium is completely precipitated in the state of peroxide by peroxide of hydrogen.

Experiment has fully confirmed this expectation; peroxide of hydrogen precipitates thorina integrally when it is in the state of chloride, and more especially when it is present as a neutral nitrate. The analogy between thorium and cerium is shown here in a striking manner. Both give peroxides in acid solution, by adding peroxide of hydrogen, and the difference depends only on the relative stabilities of these peroxides—that of cerium decomposes instantly in the presence of nitric or hydrochloric acid. It is on this very unequal stability of the two peroxides that we have endeavoured to found a method of separation. Theoretically the facts present themselves in a very simple fashion. If, to a mixture of *acetates* of Th, Ce, La, Di, and Yt, we add peroxide of hydrogen in excess, the thorium and cerium only are precipitated; the mixture Th and Ce, transformed into nitrate and treated again with peroxide of hydrogen, gives a precipitate having for its composttion Th_4O_7,N_2O_5,* the cerium remaining in solution. But when dealing with rare earths we should beware of jumping to conclusions, even those apparently the most legitimate; secondary circumstances intervene more often than would be believed, and create a veritable abyss between theory and its application.

The acetate of the peroxide of thorium is a body so gelatinous that it is impossible to filter it, and still more impossible to wash it. In the second place, the precipitation in acetic solution by means of H_2O_2 carries down, with the thorium and cerium, a small quantity of the other earths. This quantity diminishes, it is true, in proportion as the solution contains more free acetic acid; but the solubility of the cerium increases at the same time, and we thus lose in quantity what we gain in purity. An analogous phenomenon is produced when we attempt to separate thorium from cerium in nitric solution. The precipitate of the peroxide of thorium, which ought to be absolutely white, is always more or less yellow, and the more so as the quantity of cerium present in the mixture is greater. When this quantity is very small, all the thorina is not precipitated; there remains a certain quantity, very small it is true, in solution with the cerium. But in this case this double entanglement, which at first sight appears to be unfavourable, is, as a matter of fact, most favourable. So long as there remain traces of thorina mixed with the cerium, peroxide of hydrogen will

* From the *Bull. Soc. Chim.*, Series 3, vol. xix.—xx., No. 6.

* Analysis gave us per cent:—

	Calculated.	Found.
ThO	100·0	100·0
O	9·09	9·13
N_2O_5	20·45	20·45

produce, in the solution of nitrates, a precipitate easily seen on account of its large volume, and, so long as the thorium contains ever so little cerium, the filtrate will give a flocculent yellow precipitate on the addition of ammonia. These reactions are so sensitive that 0·1 per cent of thorium in cerium, or cerium in thorium, can easily be precipitated and collected on a filter.

We are thus in possession of a reagent which not only enables us to recognise the presence of very small quantities of one of these earths in a solution of the other, but also to obtain them both perfectly pure.

Purification of Cerium.—As a rule cerium only contains small quantities of thorium. In such a case we add peroxide of hydrogen to the solution of the nitrates, which has previously been evaporated to dryness or rendered neutral with ammonia, and we then heat to boiling for a few minutes. A small quantity of the filtered solution should not give any precipitate when treated with its own volume of peroxide of hydrogen and boiled again. The yellow precipitate, in the form of a voluminous yellow mass, must not be confounded with the whitish turbidity obtained by the action of peroxide of hydrogen when warmed on pure cerium; this turbidity is caused by the phosphoric acid which is always present in commercial peroxide of hydrogen, which forms an insoluble cerous phosphate, especially when heated. Cerium thus treated does not contain any trace of thorium. If the amount of thorium mixed with the cerium is at all considerable, —15 to 20 per cent, for example,—it will be of advantage to previously remove the greater part of it by means of carbonate of ammonium and ammonia. The thorina is easily soluble, and only carries a few hundredths of cerium with it. After a single treatment only, the cerium remaining insoluble contains no more than 5 or 6 per cent of ThO; it is then neutralised with HNO_3, and precipitated with peroxide of hydrogen. What we have just described for the treatment of cerium applies equally well to a mixture containing all the earths of cerite and yttria.

Purification of Thorina.—Here it is the inverse reaction that is produced; thorina is nearly always accompanied by large quantities of foreign earths, about 95 per cent in monazite.

The method to be followed depends on what we intend to do. If we wish to extract the whole of thorina existing in the mixture, it is best to treat the solution of the nitrates by peroxide of hydrogen (about 10 or 15 c.c. is necessary, supposing it to be in the proportion of 10 vols. per grm. of ThO). The thorina thus precipitated is very impure; white at first, it rapidly becomes yellow, and may even take a deep orange colour. To purify it, it is necessary to re-dissolve it in warm nitric acid, evaporate to dryness, and re-precipitate with peroxide of hydrogen. It is then almost pure, though it still gives a slight hazy incandescence, comparable with a mixture containing 0·1 or 0·2 per cent of cerium. A third precipitation makes it perfectly pure. Its purity is proved in a very simple manner; the filtrate should not give the slightest precipitate with ammonia.

In the absence of cerium, the precipitation of the thorina by peroxide of hydrogen is, in fact, complete. If we wish to work rapidly, it is of advantage to leach the nitrates several times with a neutral solution of carbonate of ammonia, the solution evaporated to dryness only needs two treatments with peroxide of hydrogen to give a thorina without a trace of incandescence.

It is necessary to remark that the impurities which are to be found in commercial peroxide of hydrogen, especially phosphoric and sulphuric acids, accumulate in the peroxide of thorium. It is therefore necessary either to distil the peroxide of hydrogen used, an operation which is not difficult by following M. Hanriot's method (*Bull. Soc. Chim.*, New Series, xliii., p. 468, 1885), or else to purify the thorium obtained. This purification is not so easy as might be believed. It is best to dissolve it in HCl, and precipitate it by oxalic acid in a strongly acid solution. We thus remove the greater part of the phosphoric acid, but not the sulphuric acid. Oxalate of thorium is unfortunately quite insoluble in boiling nitric acid: this distinguishes it from the oxalates of all the other rare earths; but, on the other hand, if it has not been previously warmed, it is instantaneously decomposed by cold caustic potash or soda, a reaction which is characteristic of it. The hydroxide thus obtained does not contain a trace of sulphuric acid. To get rid of the phosphoric acid still present, it must be re-dissolved in HCl and re-precipitated with oxalic acid, and the oxalate decomposed by soda.

The hydroxide thus obtained contains notable quantities of alkali, which cannot be got rid of by washing. It is therefore necessary to re-dissolve it in HCl, and to precipitate by ammonia. Such a hydroxide ought to be white after strong calcination, when obtained from the oxalate, nitrate, or sulphate. This degree of purity is only obtained with difficulty, for even the least traces of impurities contained in the reagents used give the calcined hydroxide a greyish or a yellowish colour, as mentioned in all previous works.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 13th, 1898.

Mr. SHELFORD BIDWELL, President, in the Chair.

A paper by Prof. W. E. AYRTON and Mr. T. MATHER, on "*Galvanometers*," was read by Prof. Ayrton. It is a sequel to *Proc. Physical Soc.*, vol. x., p. 393, and to *Phil. Mag.*, vol. xxx., p. 58.

The authors suggest that in future the comparative sensitiveness of galvanometers should be expressed in terms of the number of millimetre scale-divisions per microampère, when the observed image or "spot" is 1 metre from the mirror. Unit angular deflection is therefore 1/2000th of a radian. Further, for the periodic time,—*i. e.*, the time between two transits of the "spot" across some fixed point on the scale, in the *same* direction, —the standard should be ten seconds. It is also proposed to reduce the factor of sensitiveness, as regards resistance, to the common basis of 1 ohm. The assumption is that, for a given galvanometer, the deflection per microampère is proportional to the two-fifth power of the resistance of the windings. Tables accompanying the paper give complete data for a large number of galvanometers constructed during the past ten years, and it is possible to trace the improvements in sensitiveness throughout that time. The most sensitive galvanometers are the oscillographs; they have very short periods, the moving parts are small, the controlling fields very strong. They are designed to indicate the character of rapidly-varying currents. An oscillograph, as improved by Mr. Duddell, was exhibited; its period is 0·0001 sec., and its factor of sensitiveness, according to the authors' classification, is greater than any yet obtained. A distinction is drawn as to the use of the term "dead-beat." Maxwell applies it to galvanometers in which the motion is "aperiodic," *i. e.*, to those in which the suspended system, before coming to rest, passes only *once* through the position of equilibrium. This meaning is retained; it is not to be confused with "quick-moving" or "short-period." A pendulum illustrating these distinctions was exhibited. As regards insulation of galvanometers and shunt-boxes, the authors now apply the "guard-wire" principle of Mr. W. A. Price. The instrument to be insulated is enclosed in a metal case provided with a

terminal to which one end of the windings is connected. The second end of the windings passes out through an ebonite bush-piece. This arrangement is said to nullify leakage and to prevent electrostatic disturbance of the suspended system. In the second section of the paper, the authors calculate the limiting sensitiveness of galvanometers of the "Thomson" type. The investigation is based upon Prof. Schuster's B.A. 1894 paper; it takes into account the period of the suspended system and the specific magnetisation of the needle. Lastly, the authors discuss the relative merits of long and short periods, *i. e.*, the best "control," for galvanometers intended to indicate zero points in potentiometer operations. They conclude that if the control can be readily altered, and if the sensitiveness can be adjusted for the test, then, for rapidity of working, the "control" should be so adjusted that the sensitiveness is approximately two or three times greater than is absolutely needed for the desired accuracy.

Prof. Threlfall thought the authors' method of comparing galvanometers very misleading. The results obtained in their comparison of the oscillograph (3,310,000) and the suspended-coil galvanometer (27) might be regarded as the *reductio ad absurdum* of the proposed system. The absurdity arose from the dissimilarity of the two instruments. Moreover, the proposed system ignored the fact that sensitiveness may be obtained by optical as well as by electro-magnetic means. Optical sensitiveness, owing to its greater stability, was to be preferred to electro-magnetic sensitiveness. The fundamental problem in the construction of galvanometers is an optical one; it is necessary to decide the mass and dimensions of the suspended parts so as to ensure (1) optical accuracy, and (2) electro-magnetic sensitiveness. Thus, to some extent, the weight of the mirror determines the thickness of the suspension. As an instance of what might be done by optical methods, Prof. Threlfall referred to work done by himself and Mr. Brearley (*Phil. Mag.*, 1896), in which it was possible to measure to $1{\cdot}48 \times 10^{-13}$ ampères, and, with special refinements, to 3×10^{-14} ampères. He had found that the best diameter for glass mirrors was 1·1 c.m., with a weight just under 0·5 grm. These were used with a scale at 276 c.m., read by a microscope to 0·04 m.m. The course of the light was:—Lamp, large lens, small scale, mirror, eyepiece. The period was 25 secs., and the resistance 50,000 ohms. Even better results could be obtained by using mirrors of quarz or of blood-stone. Quartz is incomparably to be preferred to glass. Such figures indicated what could be done by optical sensitiveness—the sensitiveness that the authors ignored. It was pointed out by Prof. Threlfall that the controlling field for galvanometers of the "Thomson" type should be straight and uniform. This was best secured by using two magnets, one above and one below the needles.

Prof. Perry said the authors had not asserted that a galvanometer with higher figure of merit, according to their classification, was *superior* to another of lower figure. It must be agreed that the figure they obtain is a very valuable datum for the comparison of instruments designed for similar purposes, for instance in classifying those used by Prof. Threlfall. Mr. Duddell was to be congratulated on the extreme sensitiveness and small period of his oscillograph.

Prof. Ayrton, referring to Prof. Threlfall's *reductio ad absurdum*, admitted that the criticism would carry some conviction if the two instruments were of different kinds; if, for instance, one possessed a suspended needle and the other a suspended coil. But the argument failed, because both instrument were of the suspended-coil type. In one of them Mr. Duddell had developed the advantages to be gained by reducing the air-gap. To form an opinion of electro-magnetic improvements in galvanometers, it was necessary to reduce the results of all instruments to some system of classification. There was no objection, after that, to adding a good mirror, and reading by a good microscope.

The President proposed votes of thanks to the authors, and the meeting adjourned until May 27th.

NOTICES OF BOOKS.

Text-book of Physical Chemistry. By C. L. Speyers. New York: D. van Nostrand and Co. London: E. and F. N. Spon.

The subject-matter of this book is almost entirely confined to the relations between the various forms of energy manifested by chemical reactions and physical phenomena.

The author considers that energy exists in five principal forms, viz., mechanical, heat, electrical, magnetic, and radiant energy, with several subdivisions. He gives no place to chemical energy, as he considers this can always be identified under one or other of the above forms, and we are inclined to think he is right in so doing. His speculations—for they are nothing more—on the ultimate constitution of matter and energy are not very convincing; he apparently wishes to dispense with matter altogether, and substitute energy in its place, but, unless he attaches two separate meanings to the word energy, we cannot see that his ultimate result has any meaning. On page 2 he defines the different forms of matter as "collections of forms of energy in space."

On page 3 he states that "we need energy and a something to enable energy to collect in space before we get a material substance. This something which enables, and perhaps causes, the energy to collect in space we shall call matter."

The combination of these two leads to the puzzling statement that "We need energy and a collection of forms of energy in space, to enable energy to collect in space, before we get a material substance." We must confess that this is too deep for us.

The author, however, has not attempted to carry these speculations into the body of the book,—the persistent use of the expression "forms of energy," instead of matter, being the only indication that he has novel ideas with regard to the phenomena he is discussing.

The equations expressing the relations of energy in its various forms are well worked out from first principles in the usual manner, and many problems exemplifying their use are interspersed throughout the work.

With the exception of the first chapter, which is in places unintelligible, and the second, which is debatable, we can thoroughly recommend this work to the class of students for whom it is written.

Notes on Observations. By S. Lupton. Macmillan and Co.

This little book is intended to assist young physicists in realising the value of the results which they have obtained in physical and chemical experiments. The first six chapters, being mainly metaphysical, are rather outside the ostensible scope of the book, and call for no comment.

The rest of the book is devoted to the mathematics involved in computing the value of a series of observations, and in recording and deducing results from them. The author hardly does justice to the graphical method of recording results. Of course the curve should never be used for scaling intermediate values, if any but the roughest approximation is required.

The chapters on interpolation, snd the treatment of abnormal or doubtful results, are useful, the latter especially deserving careful attention. The principles involved in the construction of empirical formulæ are well set out in the final chapters.

On the whole we should say that, although it is in many ways unlikely to be of immediate use to beginners in experimental science, it is likely to be of great value in preparing them for what will be expected of them when they enter upon the serious business of life.

The Proceedings of the Chemical and Metallurgical Society of South Africa. May, 1894, to January, 1897. Vol. I. Edinburgh: R. W. Hunter. Johannesburg, S.A.R.: 12, Chamber of Mines Buildings.

We are pleased to welcome the first volume of "The Proceedings of the Chemical and Metallurgical Society of South Africa," comprising work done during the first three years of its existence. The subjects generally brought before the Society naturally deal mostly with gold-mining, smelting, assaying, &c.

The development of the cyanide process has attracted a good deal of attention, and many interesting and valuable papers, followed by not less valuable discussions, are to be found in these pages.

We will not here go into any further details of the work of the Society, as the reports of the monthly meetings are generally abstracted in another column as they arrive. We will conclude by offering our hearty congratulations to the Society for the plucky manner in which it keeps going ahead under most disadvantageous circumstances, hindered and trammelled as its work must be by the most obstructive Government of modern times.

The Elements of Electro-chemistry treated Experimentally. By Dr. Robert Lüpke. Translated by M. M. Pattison Muir, M.A. With 54 Figures in the Text. London: H. Grevel and Co. 1897. Pp. 223.

Of late years electricity has been making great strides in every direction, and it is now being applied more and more to chemical work; but to carry out this work in a satisfactory manner, it is first necessary for the student to be thoroughly grounded in the subject of electro-chemistry or electrolysis.

Part I. of this book is on recent theories of electrolysis. Hittorff's conception of electrolytes was that "they are salts, and are separated by electrolysis into the same atoms, or atomic groups, as the exchange in their chemical reaction with one another." All other substances, whether liquids or dissolved salts, are non-conductors. It occurred to Faraday to send the same current through several cells in series, each containing a different electrolyte; the result of this experiment was expressed in his "law of constant electrolytic action." In 1881 H. von Helmholtz, in the Faraday lecture, stated that "every single valency of an elementary or compound ion is charged with exactly the same quantity of positive or negative electricity, which behaves as if it were an electrical atom that cannot be further divided."

Part II. deals with the theory of solutions of van 't Hoff, osmotic pressure, the vapour pressure of solutions, the boiling and freezing points of solutions, &c. The osmotic theory has been of great service in the practical work of chemistry, as it has called into existence very valuable methods for determining molecular weights. In chapter 1 of this part experiments illustrating osmotic pressures are described, the results of which lead to Pfeffer's law that "The osmotic pressure of a solution is proportional to the concentration and also to the absolute temperature."

In Part III. we come to the osmotic theory of the current of galvanic cells; here the theory of Nernst, based on the propositions laid down in Parts I. and II., of the production of the electric current in galvanic cells and the deductions made from it are considered. Nernst explains the occurrence of a difference of potential between solutions of different concentrations of the same electrolyte, by the different velocities of the ions set in motion by osmotic pressure, by which means the kations become in excess in one solution and the anions in the other; these are called liquid-cells; a concentration-cell consists of two bars of the same metal, placed in solutions of a salt of the metal of different concentrations, these solutions being in contact; a current is produced until the concentrations become equalised. Reduction- and oxidation-cells are again different, and are dependent for their action on chemical energy, which is transformed into electrical energy. Chap. 5 of Part III. is on the solution-pressures of the metals, and to arrange the metals in their order of solution-pressure it is only necessary to determine whether one metal is able to precipitate another from a solution of one of its salts, and thus, because of its greater solution-pressure, draw away the electrical charges to the kations of the second metals.

A few chapters on intensity of fixation and polarisation, irreversible cells, accumulators, and the energetics of galvanic elements, close a most interesting and clearly written volume, on which the author is to be congratulated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 15, April 12, 1898.

The President announced the death of M. Aimé Girard, Member of the Section of Rural Economy. The meeting was adjourned in consequence.

Observations relative to the Action of Oxygen on Sulphide of Carbon and to the Chemical Influence of Light. Preliminary Work to Determine the Reactions.—M. Berthelot.—After some introductory speculative remarks the author gives a general idea of his experiments. A sealed tube containing about 1 grm. of sulphide of carbon is placed in a flask of 2·5 to 3 litres capacity, large enough for the vapourised sulphide of carbon to fill at a temperature of 15°. The neck of the flask was then contracted and sealed, and the small tube broken by careful shaking. Three such flasks were prepared; two were left on the laboratory table in bright light, but away from direct sunlight; the third was placed unsheltered on the roof. The experiment lasted 379 days, when the flasks were examined. The first contained 1·055 grm. of CS_2; the glass was quite clear, and no sulphur was deposited; no carbonic acid was found, but there was a little gas present which turned out to consist of O = 20·7 and N = 79·3. The second flask (also kept in the laboratory) behaved similarly, but the residual gas had the composition O = 20·9 and N = 79·1, but in neither case had the CS_2 undergone any change. The third flask, on the roof, containing 1·07 grm. of sulphide of carbon exposed to all weathers and direct sunlight, was quickly acted upon; after only a few hours a white or yellowish deposit formed on the interior surface of the glass, and this increased progressively; at the end of the year the gas was found to consist of—

	Per cent.
CO_2	1·5
CS_2	8·5
CO	2·3
O	14·7
N	72·0
Water vapour	1·0
	100·00

The solid matter was found to consist of—

	Grm.
Sublimed sulphur	0·104
Carbonaceous matter..	0·030
Carbonic acid	0·0024
Sulphide of carbon and unestimated matter	0·0136

Absorption of Oxygen by Pyrogallate of Potash.—M. Berthelot.—Experiments were carried out on solutions of widely varying strengths of pyrogallol and of potash, and even with solid potash, but always according to exact equivalents, from ½ equivalent of potash up to 3, and further from the ordinary up to high temperatures. The paper is too long to usefully abstract in a short space.

Rays Emitted by Compounds of Uranium and of Thorium.—Mdme. S. Curie.—Two plates were arranged as a condenser, one of them being covered with a uniform layer of uranium or other substance finely powdered. A difference of potential of 100 volts was established between the two plates, which were kept at 3 c.m. apart; a large number of metals, salts, oxides, and minerals were experimented on to find out if any of them had, like uranium, the power of making air a conductor of electricity. This was found to be the case. It was noticed that the more uranium present in any of its salts, the more active that salt was; the compounds of thorium are very active, while oxide of thorium surpasses that of even metallic uranium. It is noticeable that uranium and thorium are, of the elements tried, both the most active and also have the highest atomic weights. Good photographic impressions have been obtained with uranium, uranous oxide, pitchblende, chalcolite, and oxide of thorium. These bodies will act through air, glass, or aluminium.

The Combinations of Pyridine and of Trimethylamine with Formic and Acetic Acids.—G. André.—The author has followed up his researches on the compounds formed by formic, acetic, or propionic acids with pyridine. He has now gone further, and finds that the combinations between trimethylamine and formic and acetic acids are much more stable than those formed by pyridine with the same acids. The formic compound has the same type of formula as that obtained with pyridine, but the acetic compound is much richer in acid. These two combinations with trimethylamine both have a notably higher boiling-point than either of their components.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 4.

Separation and Estimation of Lead, Copper, and Arsenic.—F. Jean.—Already inserted.

Some New Derivatives of Homopyrocatechin.—H. Cousin.—Homopyrocatechin has been but little studied up to the present time, and, with the exception of a few ethers, none of its derivatives are known. By acting on 1 molecule of homopyrocatechin with 1 molecule of iodide of methyl in the presence of potash, a mixture of creosol, $CH_3—C_6H_3—\overset{(3)}{O}CH_3—\overset{(4)}{O}H$, and its isomer, $CH_3—C_6H_3—\overset{(3)}{O}H—\overset{(4)}{O}CH_3$, was obtained. Iodide of methyl in excess gives homoveratrol, $C_7H_6—(OCH_3)_2$. Iodide of ethyl gave analogous results. By treating homopyrocatechin in acetic solution with a current of chlorine, two chlorinised bodies were obtained:—$C_7H_5Cl_3O_2+2H_2O$, in white needles, losing its two molecules of water *in vacuo*, and melting at 179—180°; and chlorinised methylorthoquinone, $C_7H_3Cl_3O_2$, crystallising in small bright red microscopic plates slightly soluble in alcohol, more so in acetic acid, and melting at 97—98°. Reducing agents change this substance to $C_7H_5Cl_3O_2$. Analogous bodies are formed by the action of bromine.

The author has also isolated two mononitrated homo pyrocatechines and the corresponding homoveratrols. 5-Nitrohomopyrocatechin, $C_7H_7O_2—NO_2$; 5-nitrohomoveratrol, $C_7H_5—(OCH_3)_2—\overset{(5)}{N}O_2$; and 6-nitrohomopyrocatechin, $C_7H_5—(OH)_2—\overset{(5)}{N}O_2$; 6-nitrohomoveratrol, $C_7H_5—(OCH_3)_2—\overset{(6)}{N}O_2$. The action of sulphuric acid on homopyrocatechin gave only one sulphur derivative, viz., homopyrocatechin monosulphonic acid, $C_7H_5—(OH)_2—SO_3H$. It is a deliquescent crystalline mass, very easily soluble, melting at 93—94°. The potash salt crystallises in fine needles, and is soluble in water and in boiling alcohol. Heated in a sealed tube with iodide of methyl and alcoholic potash, it gives a homoveratrol sulphonate of potassium, $C_7H_5—(OCH_3)_2—SO_3K$.

Zeitschrift fur Analytische Chemie.
Vol. xxxvii., No. 2.

Some Contributions to the Chemistry of Proteid Precipitates.—H. Schjerning.—The author examines the proteid precipitates obtained from beer, Merck's diastase, Witte's peptone, egg albumen, and milk. He uses chlorides, acetates, and sulphates of the metals Pb, Cu, Hg, Mg, Fe, Ca, Sr, Ba, Zn, Co, and Mn, and obtains precipitates, which are washed with water and weighed. He is unable to obtain precipitates of the noble metals quantitatively, probably owing to the ease with which the oxide is reduced to the free metal.

Method of Determining the Fineness of Meal.—Dr. Victor Vedrödi.—It has already been shown that the fineness of meal is proportional to the ash content, and the author gives a simple method of determining this ash content. He takes six crucibles containing about 5 grms. of meal and heats them for 6 to 8 hours in a Fletcher's muffle oven, cools them in a desiccator, and weighs again. By adding a little HCl and extracting with water the ash can be examined and estimated.

Colorimetric Determination of the Weight of Smoke.—Dr. P. Fritzsche.—This is usually determined by allowing a measured volume of the gas from the chimney to pass through a glass tube prepared with asbestos, and estimating the obtained carbon as CO_2. This method, however, is lengthy, and has to be done in a laboratory. The author has devised a simple method, in which a tube is prepared with loose cellulose to collect the soot. This is connected on one side with another tube, which can be inserted in the chimney, and on the other side with an aspirator. About 10 to 20 litres of gas are drawn in by the aspirator. The cellulose and soot are placed in a flask with 200 c.c. of water and well shaken till the colour is a uniform grey. This is compared with standard colours obtained by shaking up the same quantity of cellulose with 5, 10, 15, 20, 25, and 30 grms. of soot in 200 c.c. water. After a little experience these soot determinations can be performed accurately in a few minutes.

Investigation of Commercial Incandescent Bodies.—E. Hintz.—The author analyses 40 specimens, and finds that they all consist chiefly of thorium, with a small percentage of cerium oxide and varying traces of neodymium, yttrium, zirconium, lime, magnesia, and silica. He then investigates photometrically incandescent substances containing known proportions of the various earths, and comes to the conclusion that if they contain approximately 99 parts of thorium to 1 part of cerium, oxides of neodymium, lanthanum, and yttrium up to 1 per cent do not influence the lighting-power, while the influence of 0·1 per cent of zirconium is uncertain.

MISCELLANEOUS.

Royal Institution. — On Tuesday next, May 31st, Professor S. H. Butcher begins a course of two lectures at the Royal Institution, on "Literary Criticism in Greece"; on Thursday, June 2nd, Dr. Edward E. Klein delivers the first of two lectures on "Modern Methods and their Achievements in Bacteriology"; and on Saturday, June 4th, Dr. Richard Caton begins a course of two lectures on "The Temples and Ritual of Asklepios at Epidaurus and Athens" (with lantern illustrations). The Friday Evening Discourse on June 3rd is by Professor W. M. Flinders Petrie, on "The Development of the Tomb in Egypt"; that on June 10th is by Lord Rayleigh, whose subject is "Some Experiments with the Telephone."

On the Assay of Minium.—At the Second International Congress of Applied Chemistry, M. Forestier made the following communication in view of the adoption of a uniform method of commercial assays. According to him, the value of a minium depends on its percentage of pure minium, Pb_3O_4, and the percentage of impurities. Forestier proposes to estimate the latter in the following manner:—10 grms. of minium are treated in a flask, with 10 grms. of ordinary sugar dissolved in 50 or 60 c.c. of boiling water, and 10 c.c. of nitric acid at 36°, until the red colour has entirely disappeared. If there is much residue the mixture must be heated for a quarter of an hour. The insoluble matter is collected on a tared filter and weighed. To estimate the Pb_3O_4, the author treated the 1 grm. of the substance with acetic acid; this decomposes the oxide, leaving a residue of PbO_2: he used 10 c.c. of acid at 10°, and 20 c.c. of water, heated for half an hour on the water-bath, and collected the binoxide. The weight of this is determined either by direct weighing or titrimetrically by the iodine process. It should be noticed that the author replaces the nitric acid generally used by acetic acid; according to him the former dissolves a part of the binoxide. The Congress admitted the Forestier process.—*Zeit. f. Ang. Chem.*, 1898, No. 11, p. 176.

MEETINGS FOR THE WEEK.

TUESDAY, 31st.—Royal Institution, 3. "Literary Criticism in Greece," by Professor S. H. Butcher, LL.D.

THURSDAY, June 2nd.—Royal Institution, 3. "Modern Methods and their Achievements in Bacteriology," by Edward E. Klein, M.D., F.R.S.

—— Chemical, 8. "The Action of Ether on Organic Acids and on Carbohydrates in presence of Hydrogen Bromide," by H. J. H. Fenton, M.A., and Mildred Gostling, B.Sc.

FRIDAY, 3rd.—Royal Institution, 9. "The Development of the Tomb in Egypt," by Professor W. M. Flinders Petrie, D.C.L.

SATURDAY, 4th.—Royal Institution, 3. "The Temples and Ritual of Asklepios at Epidaurus and Athens," by Richard Caton, M.D., F.R.C.P.

TO SPIRIT DISTILLERS, BREWERS, MANUFACTURING CHEMISTS, AND OTHERS.

MESSRS. FULLER, HORSEY, SONS, & CASSELL are instructed to SELL by AUCTION, in lots, at the Distillery, 159, Blackfriars Road, S.E., on Tuesday, June 14, 1898, at 12 o'clock precisely, DISTILLING PLANT and MACHINERY, including a 585 gallon copper rectifying still, one 1623 and one 995 gallon copper pot stills, three copper worms, two circular cast-iron worm tubs, two copper spirit safes, copper piping and gun-metal cocks, copper boiling pan, set of three throw gun-metal pumps, three lift and force pumps, Cornish and vertical boilers, table engine, iron steam and water piping, 75 oak spirit vats and casks, copper measures, cranes, and utensils, two useful horses, four pair and single horse vans, harness, stable utensils, office furniture, and other effects. May be viewed the day preceding, and catalogues had on the premises; and of Messrs. Fuller, Horsey, Sons, & Cassell, 11, Billiter Square, E.C.

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FACULTY OF SCIENCE.

RESEARCH SCHOLARSHIPS.

(Founded by the late T. Aubrey Bowen, Esq., of Melbourne, Australia).

(*a*) Two BOWEN SCHOLARSHIPS in ENGINEERING, each of the value of about £96.
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Further particulars may be obtained on application to the REGISTRAR.

TO MANUFACTURING CHEMISTS AND OTHERS.

The LONDON COUNTY COUNCIL is prepared to receive Tenders for the Supply of 5550 tons of PROTO-SULPHATE OF IRON (Commercial Green Vitriol) to the Barking Outfall Works, near Beckton, North Woolwich, and the Crossness Outfall Works, near Erith, Kent.

Persons desiring to submit tenders may obtain the specifications, form of tender, and other particulars at the Engineer's Department, County Hall, Spring Gardens, S.W. Tenders must be upon the official forms, and the printed instructions contained therein must be strictly complied with. The contractors will be required to pay to all workmen employed by them such wages and to observe such hours of labour as are generally accepted as fair in the trade. Tenders are to be delivered at the County Hall in a sealed cover addressed to the Clerk of the London County Council, and marked "Tender for Proto-Sulphate of Iron, Barking and Crossness Outfalls." No tender will be received after 10 a.m. on Tuesday, the 21st June, 1898. Any tender which does not comply with the printed instructions for tender may be rejected.

The Council does not bind itself to accept the lowest or any tender, and it will not accept the tender of any person or firm who shall on any previous occasion have withdrawn a tender after the same has been opened, unless the reasons for the withdrawal were satisfactory to the Council.

C. J. STEWART,
Clerk of the Council.

Spring Gardens, S.W.,
24th May, 1898.

TO LIME MERCHANTS AND OTHERS

The LONDON COUNTY COUNCIL is prepared to receive Tenders for the Supply of 23,800 tons of LIME to the Barking Outfall Works, near Beckton, North Woolwich, and the Crossness Outfall Works, near Erith, Kent.

Persons desiring to submit tenders may obtain the specifications, form of tender, and other particulars at the Engineer's Department, County Hall, Spring Gardens, S.W. Tenders must be upon the official forms, and the printed instructions contained therein must be strictly complied with. The contractors will be required to pay to all workmen employed by them such wages and to observe such hours of labour as are generally accepted as fair in the trade. Tenders are to be delivered at the County Hall in a sealed cover addressed to the Clerk of the London County Council, and marked "Tender for Lime, Barking and Crossness Outfalls." No tender will be received after 10 a.m. on Tuesday, the 21st June, 1898. Any tender which does not comply with the printed instructions for tender may be rejected.

The Council does not bind itself to accept the lowest or any tender, and it will not accept the tender of any person or firm who shall on any previous occasion have withdrawn a tender after the same has been opened unless the reasons for the withdrawal were satisfactory to the Council.

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2010.

ON ATOM FORMS, AS DEDUCED FROM THE CRYSTALLINE MODIFICATIONS OF THE ELEMENTS.*

By WM. L. T. ADDISON, B.A., M.B.

The relationships outlined in this paper are too large and many to be fully discussed in the space allotted.

That such a difficulty may be somewhat met it was thought advisable to treat the greater portion of the subject in outline merely, stating as facts such as may be demonstrated by observation or geometric proof, and to discuss at greater length the simplest of crystalline allotropic elements—phosphorus.

In the study of crystallography, one's attention reverts to those substances which are most common and most crystalline in character. Of such substances, calcite has been selected by observer after observer, from the time of Nicholas Steno down to the present. Among the workers in this science was Mitscherlich, who observed that similar chemical compounds had the same form and could intercrystallise in the same crystal. Thus, calcium, magnesium, manganese, ferrous and zinc carbonates crystallise and intercrystallise in rhombohedra of approximately the same proportions. Thus, form is consequent on the chemical grouping, and is a function of that group of atoms.

There is in the carbonate group a central atom carbon, about which the other atoms are grouped; and these outer atoms are the outer portions of the molecule, or those of easiest and first contact.

The grouping is at four attractive places, and the form of the crystal being constant, the form of the molecule and the position of these areas of attraction must also be constant.

Of carbon we may know much. It occurs in crystalline form, as the diamond, sp. gr. 3·6; and as graphite, sp. gr. 1·8 when pure, or one-half the specific gravity of the diamond.

The cleavage of the diamond is in regular octahedra; that is, the line of union of the carbon atoms lie in octahedral planes. This form may be given either by octahedra being placed edge to edge, or by tetrahedra similarly placed, or by an arrangement of the two together, in which they would fill space. It could not be an arrangement of both forms, and so must be of one of the forms. The tetrahedron has the same number of solid angles or prominences and the same number of faces as the carbon atom has areas of valence. In the octahedron, the differentiated portions are six solid angles and eight faces. Thus the differentiated portions of the tetrahedron are coincident in number with the chemical attractions of the carbon atom. If the carbon atom be a regular tetrahedron, then—in the arrangement described—the solid angles are the differentiated portions in contact, and they may be regarded as the areas of attraction.

If a series be taken in a diagonal axis of symmetry of the octahedral grouping, it is composed of two hexagonal series of regular tetrahedra, with their apices pointing in opposite directions. If one series be taken away, the atoms of the remaining series will be left with their solid angles only in contact; the specific gravity will be half that of the diamond or octahedral grouping, and the arrangement will account for a rhombohedral, a hexagonal, and a gross form simulating a monoclinic one, the basal plane of which is at approximately 70° + to the oblique axis; it also will account for the intermolecular mobility of graphite, and the triangular markings on the basal plane of that mineral.

Silicon, germanium, lead, and thorium occur in regular octahedra, as does carbon.

Tin, titanium, and zirconium dioxides are isomorphous, and tin is known to occur in quadratic octahedra, and may be accounted for as a grouping of quadratic tetrahedra.

Zirconium has been observed in tin-white microscopic monoclinic leaflets. Such leaflets occur in series parallel to P faces of the octahedra described for tin.

If the prominences or solid angles of the outline forms of all atoms be their areas of valence, as in carbon, phosphorus requires an outline form of five solid angles. Such a form is found in the bi-pyramidal hexahedron. Phosphorus occurs in two crystalline forms—1st, as regular octahedra and rhombic dodecahedra, of sp. gr. 1·826 to 2·089; and 2nd, as rhombohedra, of sp. gr. 2·34. That there is a regular form is a significant fact, which leads one to expect some regular characteristics in the primal form.

If the solid angles of the bi-pyramidal hexahedron (and we will in future refer to the outline form of the atom as a solid one) be arranged with three equidistant solid angles in a zone, and two apiceal solid angles, one upon either side of, and equidistant to, the plane of the zone, and at the same distances from the zonal angles, as the zonal angles are apart *inter se*, then a form is given composed of two regular tetrahedra, base to base, and of regular characteristics.

Such a form may be arranged with its edges together in two ways:—1st, With two apiceal solid angles opposite and symmetrically three zonal solid angles about the point of contact to give a rhombohedral form; and, 2nd, with eight apiceal solid angles about a point, and the zonal angles in pairs.

In the first arrangement, the angle R is 82° 18′ +. In a continuous arrangement, columnar interatomic spaces are observed. These are as of regular octahedral spaces face to face. Thus, the upper and lower faces of these hypothetical octahedra are in apposition with those of the octahedra above and below. The remaining six faces are in apposition with the faces of the hexahedra, and each hexahedron has all its faces in apposition with those of octahedra; hence the proportion in number of octahedra to hexahedra is as the faces of each form in apposition with those of the other, or as one to one.

A regular octahedron of 2 inch edge is composed of two pyramids of base area 4 square inches and of $\sqrt{2}$ inches height, so that by the formula—

$$\text{The solid contents of a pyramid} = \frac{\text{Area of base} + \text{height}}{3}$$

its solid contents are—

$$\left(\frac{4}{3} \times \sqrt{2}\right)2 = 8\frac{\sqrt{2}}{3} \text{ cubic inches.}$$

An octahedron of 4 inches edge has a cubic area—

$$\left(\frac{16}{3} \times \frac{2\sqrt{2}}{1}\right)2 = \frac{64\sqrt{2}}{3} \text{ cubic inches.}$$

Such an octahedron is composed of six octahedra and eight tetrahedra of 2 inch edge. The six smaller octahedra have an area of—

$$\frac{48\sqrt{2}}{3} \text{ cubic inches,}$$

therefore the remaining eight tetrahedra have an area—

$$\frac{16\sqrt{2}}{3} \text{ cubic inches,}$$

* Abstract of a Paper read before the British Association (Section B), Toronto Meeting, 1897.

and each tetrahedron has an area—

$$\frac{2\sqrt{2}}{3} \text{ cubic inches.}$$

The hexahedron has an area of two tetrahedra, or—

$$\frac{4\sqrt{2}}{3} \text{ cubic inches,}$$

and the area occupied per hexahedron in the rhombohedral arrangement is its own area + that of an octahedron $= \frac{12\sqrt{2}}{3} = 5{\cdot}6568$ cubic inches.

In the second or regular arrangement, in which eight apiceal solid angles meet about a point, the remaining apiceal solid angles form the solid angles of an outline cube, and the two opposite solid angles of the cube are apart—twice the distance between the apices of the hexahedron. If x = the edge of the cube, then the diagonal of its face is $x\sqrt{2}$, and the line between the two opposite solid angles $= \sqrt{(\text{edge})^2 + (\text{diagonal of face})^2} = x\sqrt{3}$; therefore, $x\sqrt{3} = 2$ (length of the hexahedron).

The length of the hexahedron may be found as follows:—The zone of the hexahedron is an equilateral triangle of 2 in edge. Bisect each side, and join the points of bisection to the opposite angles, thus bisecting the angle 60°. There are then six triangles, each one-half of an equilateral triangle of sides, y; y = hypotenuse, or the line from the centre of the zone to the zonal angle. The other sides of the triangle are 1 and $\frac{1}{2}y$, so—

$$1 + \tfrac{1}{4}y^2 = y^2 \text{ and } \tfrac{3}{4}y^2 = 1,\ y = \frac{2}{\sqrt{3}}$$

On the triangle of the line y, the line from the centre of the zone to the apex of the hexahedron, and the edge of the hexahedron joining these lines, let z = the line dropped from the apex of the hexahedron to the centre of its zone, then—

$$z^2 + y^2 = 4,\ z^2 + \tfrac{4}{3} = 4,\ z^2 = \tfrac{8}{3} \text{ and } z\ \frac{2\sqrt{2}}{\sqrt{3}}$$

and the length of the hexahedron is—

$$\left(\frac{2\sqrt{2}}{3}\right)2 = \frac{4\sqrt{2}}{\sqrt{3}} \text{ inches.}$$

In the cube of edge x,—

$$x\sqrt{3} = \frac{8\sqrt{2}}{\sqrt{3}}\ x = \frac{8\sqrt{2}}{3},$$

and 8 hexahedra occupy—

$$x^3 = \left(\frac{8\sqrt{2}}{3}\right)^3 \text{ cubic inches,}$$

and 1 hexahedron occupies—

$$\frac{(8)^3 \times 2\sqrt{2}}{3} = 6{\cdot}6987 \text{ cubic inches.}$$

The specific gravities of these allotropic modifications should be inversely according to their space occupation. Thus, the regular form should have a specific gravity—

$$\frac{2{\cdot}34}{1} \times \frac{5{\cdot}6568}{6{\cdot}6987} = 1{\cdot}976.$$

The mean of the observed specific gravities is—

$$\frac{1826 + 2089}{2} = 1{\cdot}957.$$

The difference between the estimated and mean results thus is less than the variations of observation.

Phosphorus also occurs in a very stable amorphous form, and, as such, might be accounted for by hexahedra face to face, so that two zonal and two apiceal solid angles are in apposition. In such a grouping, continuous form is impossible. Its sp. gr. varies from 1·964 to 2·293 at ordinary temperatures.

The rhombohedral form, or that form in which the different sort of solid angles are in contact, is the most stable form, and one acting chemically with difficulty. The regular form very easily enters into chemical action. That the rhombohedral form is the most stable is a most significant fact.

The valence of phosphorus toward oxygen, sulphur, and chlorine is five; toward hydrogen, three. All the areas of valence are available to oxygen, and but three to hydrogen. Hydrogen is an electro-positive element, and the area to which it is attached must be electro-negative in sort. The two remaining angles or areas of valence do not attract hydrogen, and so are of similar electro-condition. Thus there are angles three of a sort and two of a sort in form, and three of a sort and two of a sort in valence or electro-condition; and an arrangement in which the three of a sort were in junction with the two of a sort in form, is more stable than an arrangement in which the three of a sort are grouped together, and the two of a sort in form together. Is it not a fair inference that the three of a sort in form are the three of a sort in valence or electro-condition, and, similarly, the two of a sort in form the two of a sort in electro-condition, and that the zonal angles are electro-negative and the apiceal electro-positive, and that the angle nearer the centre is electro-negative to the more distant one?

Arsenic, antimony, and bismuth occur in rhombohedra with an increasing angle R. Arsenic and antimony occur rarely in the regular form.

Sulphur has a valence of six, and would thus have a primal form of six solid angles. Of such a form are octahedra. If octahedra be placed with their similar edges together, so that if there be any difference of solid angles different sorts are in apposition, they will reproduce themselves in gross form. Sulphur occurs in rhombic octahedra of sp. gr. 2·05, and axes 1, 1·23, 2·344, and so we may assume the atomic form to be of these proportions. Sulphur also occurs in a form said to be monoclinic, but really in a diclinic form.

This modification occurs at higher temperatures than the rhombic one, is of sp. gr. 1·96, and at ordinary temperatures reverts with the evolution of heat to the rhombic form. It occurs in brilliant, yellow, transparent, columnar crystals of oblique, basal cleavage. Thus the diclinic form of sulphur is in a condition of strain, has a slight lowering of specific gravity, has interatomic spaces through which the atoms rotate to assume the rhombic arrangement, and the primal form must account for these properties in such a way that the specific gravities are inversely to the space occupied per form. These primal forms may be placed face to face, with different zonal and solid angles in apposition, as in the rhombic arrangement. In this case the apiceal solid angles diverge, and make continued form impossible. If these become convergent, the zonal angles are slightly displaced, and so in strain; the zonal edge of the atom form becomes less oblique to the lines of fission into series, thus thickening the series 1/20·3, approximately the observed proportionate decrease of specific gravity. In such an arrangement there are spaces permitting the forms to diverge, until their long axes become parallel to assume the rhombic arrangement. The arrangement face to face, as described, gives a diclinic columnar form of oblique basal cleavage.

Selenium has modifications similar to those of sulphur. Tellurium occurs in rhombohedra, and might be accounted for by regular octahedra placed face to face. This view is supported by its isomorphism with the regular elements, gold and silver. The hydrides of these elements will be discussed in connection with that of chlorine.

In sulphur the number of atoms necessary to give a complete rhombic and diclinic group, is the number of atoms found in their respective gas molecules. The six-atom group occurs at a lower temperature than the

two-atom group, in both crystalline and gaseous conditions.

Iodine crystallises from the molten state in foliated masses, tenacious in two planes, and easily fissile in the third, to give plates showing striæ intersecting at angles of 70°. Thus is shown a slight attraction in one axis, and a very much stronger attraction in the other, or those in which the series are at 72° to each other.

Iodine may be seen under the microscope to crystallise (from its solutions in diethyl ether and chloroform) in rhombic octahedra and platelets, in needles, and in roughly rhombic retiform combinations. The octahedra occur in slowly evaporating concentrated solutions, and their like edges meet over the most acute solid angle, at 72° and 54° respectively. The platelets occur in more rapidly evaporated solutions, and in company with octahedra or needles, according to the slowness of the evaporation. The platelets have angles 72° and 108°, and the acute angles of one platelet when it comes in the vicinity of another platelet shows an attraction and choice for the obtuse angles of the other platelet, and *vice versâ*.

The needles occur in the more rapidly evaporating solutions. If in a solution two needles, from opposite directions, project themselves toward the same point, as they approach they cease their self-projection, and thicken themselves while there remains iodine in solution. Should, however, a needle project itself toward the more central portion of another needle, it will continue to grow towards and will join the other needle at an angle 72° or 36°. The needle may even take a curved course to arrive at that angle, and will remain curved until the solvent is evaporated, after which it assumes a straight form. While the crystal is taking the iodine from the solution, the colour is seen to go at first slowly, and decrease with accelerated velocity, until it disappears almost instantaneously, while there yet remains present some of the solvent. The rhombic retiform body is cast down on still more rapid evaporation, and consists of bars of iodine which appear fine under 450 D enlargement. If this form be permitted to evaporate, as the bars which connect some outer bar volatilise, and the outer bar is not held off by intervening bars, the outer bar springs with great velocity to the inner portions of the retiform body, showing an attraction at sensible distance.

Iodine has a valence of seven, and so its atom form may be accounted for by a bipyramidal dekahedron,—that is, a form of seven solid angles. Its symmetric form would be of five zonal angles at equal distances apart, and two apiceal angles, one upon either side of and equidistant from the zone, and each apiceal solid angle equidistant from the zonal solid angles. If such a form be placed with a zonal edge in apposition with the zonal edge of another form, and their zonal planes in the same plane, a rhombic group of angles 108° and 72° in the zonal plane results. These groups may be so arranged that they give a gross form of these proportions. If such a layer of atoms be placed over a layer, but with one series less than the layer beneath, so that the apiceal angles of each layer are in contact, and layer be placed over layer with a similar decrease of series, the half of an octahedron will be formed. If the primal form have its apiceal solid angles the same distance apart as the zonal angles, and the other half of the octahedron as above described be built, an octahedron, in which similar edges over the most acute solid angle will make 72° and 5 yards of an angle, will result. Such an arrangement permits of union of single attractive areas in the one axis, and five attractive areas in the other two axes, thus accounting for the easy fission into tenacious layers of angles 72° and 108°.

The hydrides of this group are monohydrides. There are compounds of the formulæ Ag_2Cl and K_2Cl, showing a bivalence toward elements of Group I. of Mendeleeff's Table, and two particularly electro-negative areas of valence, or of the series which corresponds in number with those, which may be shown in iodine to be nearest the centre of the atom. The satisfaction of one of these areas of valence satisfies the opposite one. If such a condition holds true in sulphur, then the hydride of sulphur would be the observed one, sulphur dihydride.

The elements of Group VIII. have a valence of four, and so would, if the primal form be a regular tetrahedron, give rise to regular forms. Such crystal forms as have been observed are of regular sort. There may be shown certain reasons to believe that both oxygen and sulphur may have a monovalent action, and that in osmium and iridium tetroxides the oxygen is monovalent.

The remaining Groups of Mendeleeff's Tables, III., II., and I., would have as primal forms a triangle of thickness, a rod form, and a spherical form, respectively. The triangular form in aluminium may be shown to be equilateral, in that two atoms are attached by three atoms of oxygen, and these outlying points formed by the oxygen atoms, when grouped, give a hexagonal form, which must be dependent on equilateral triangular subforms, the grouping of which is dependent on the central or aluminium atoms, which dictate the arrangement. These triangles may lie in the planes of the faces of the tetrahedra when arranged in the diamond grouping.

The atoms of the elements of Group II. add themselves up to give, first, equilateral triangles; and second, these triangles to give either regular or hexagonal groups. Both regular and hexagonal forms occur in zinc, and the hexagonal in beryllium. Cadmium and mercury occur in the regular system.

The atoms of Group I. may unite, first, in rods of two atoms; second, in a rod of two rods of the first sort; third, three rods to form an equilateral triangular body; and fourth, these triangles together to give a regular form. These four steps are curiously coincident in number with the four allotropic modifications of silver, the first being smallest and easiest of solution, the second more difficult of solution, the third more stable in form, and the fourth the most stable of arrangements.

Malleability has a coincidence with atomic forms, permitting of interatomic mobility in their arrangement. Thus the atoms of carbon are of regular tetrahedral form, and any loose solid angle is as an apex to a tripod, of equal limbs. Hence the stability of form and the rigidity of the diamond. If one angle of an aluminium atom become free, it may, unless checked by some other atom, rotate circularly about a line joining the two remaining angles. Thus aluminium shows a marked interatomic mobility, by its malleability, and its tendency to a variable crystal form. If, in an atom of an element of Group II. of Mendeleeff's Table, one of its two areas of attraction be free, it may, unless checked by some other atom, rotate spherically about its stationary area of attraction. The interatomic mobility of such elements is shown by their increase of malleability over the elements of Group III. The interatomic mobility and malleability of the elements of Group I. are increased over those of Group II. by a joint in their rod form.

There is another factor in interatomic mobility—the intensity of attraction. If chemical and crystal attractions be different manifestations of the same attraction, then with the decrease of chemical activity there will be a decrease of rigidity and stability of form, with an increase in interatomic mobility and malleability.

The preceding relations are well shown in the following comparisons:—

- The diamond.—Very crystalline, brittle, and hard.
- Tin.—Malleable, breaking with crystallline structure.
- Lead.—Soft and malleable.
- Iron, nickel, and cobalt.—Brittle as compared with platinum.
- Magnesium, zinc, cadmium, and mercury.—Increasing in softness, with increase of atomic weight and decrease of chemical activity.
- Copper, silver, and gold.—Increasing in malleability with increasing atomic weight and decreasing chemical activity.

Thus is given a set of relations evidencing the unity of chemical and crystal attractions.

It is probable that, at no distant day, we will be able to determine the causes of the different physical properties of different sorts of matter, and that, in the determination of these causes, form will bear no insignificant part.

In closing this very incomplete sketch it might be well to add that, within a short time, the original paper will be published in full.

Byng Inlet, Ontario, Canada.

ON THE

SEPARATION OF THE OXIDES OF CERIUM AND THORIUM.*

By G. WYROUBOFF and A. VERNEUIL.

(Concluded from p. 246).

Estimation of Cerium in the presence of other Rare Earths.—The methods we have described enable us to separate cerium quantitatively, with an accuracy superior to that of all previously known methods. It has the further advantage of not requiring much of the substance to be analysed.

Estimation in presence of Lanthanum, Didymium, and the Rare Earths of Yttria.—If the mixture of the oxides from the calcination of the oxalates was entirely, or only partially, soluble in nitric acid (which shows that it contains more than 50 per cent of cerium), it becomes easily soluble by the addition of small successive quantities of peroxide of hydrogen. A disengagement of oxygen, and the reduction of the cerosoceric oxide, takes place. To the more or less violet limpid solution we add peroxide of hydrogen (10 c.c. per grm. of the oxide), then ammonia until alkaline, and boil to transform the brown precipitate into the clear yellow cerosoceric hydrate. This transformation is complete when there is no longer any disengagement of oxygen. The solution is then filtered and washed, to get rid of the nitrate of ammonia which is formed by the last reaction. Dry at 110°, and detach the filtrate from the paper as carefully as possible; the filter must be incinerated and calcined, and the residue treated with a few drops of HNO_3 hot, and peroxide of hydrogen, and then evaporated to dryness. It is taken up with a little water and added to the solution of the bulk of the precipitate, which must be dissolved in warm nitric acid. This solution is evaporated down to a syrup, taken up with a few c.c. of water, and again evaporated to dryness. On cooling, a vitreous mass of a deep yellow colour is obtained; this is dissolved in 100 c.c. of a 5 per cent solution of NO_3NH_4, and heated to about 70°; the yellow liquid begins to get clouded, a yellowish white precipitate forms, and the reaction is finished when the supernatant liquor takes the violet tint of the didymium salts. After filtering, the precipitate is washed with a 5 per cent solution of NO_3NH_4 and calcined. We thus obtain 75 or 85 per cent of the cerium present in the mixture, in a perfectly pure state. The filtrate is precipitated by oxalate of ammonia, of which much excess should not be used, the oxalates of Ce, La, and Di, contrary to the general opinion, being very slightly soluble. The solution is made alkaline by a few drops of ammonia. The oxalates, which do not need to be washed, are calcined; this time they are all soluble in HNO_3. On repeating the above operation one can obtain several hundredths of pure cerium. The filtrate contains the rest of the cerium and all the other earths; these are re-converted into oxalates and calcined. The substance is then dissolved in HNO_3, a few drops of peroxide of hydrogen added to reduce the cerium, and then evaporated to dryness. To the solution of the nitrates we add acetate of soda, and precipitate by a large excess of peroxide of hydrogen (about 10 c.c. of water). The liquid must be slightly warmed to hasten the deposition of the precipitate, which contains all the cerium as well as a small quantity of the other earths. It is then washed with water to which a few drops of peroxide of hydrogen have been added. The filtrate is then precipitated either by oxalate of ammonia or by ammonia. The following figures show the degree of exactness possible by this process:—We took 1·242 grms. of a synthetic mixture, containing 0·3718 grm. of Ce_3O_4 and 0·8702 grm. of other earths, such as are found in monazite after the elimination of the thorina and cerium.

1st precipitation	..	0·3160 pure Ce_3O_4.
2nd ,,	..	0·0175 ,,
3rd ,,	..	0·0485 Ce_3O_4+LaO,DiO.
		0·3820

Thus we recovered the cerium with a surcharge of 2·68 per cent, due to the entanglement of the other earths in the precipitation by peroxide of hydrogen in acetic solution.

Estimation in the presence of Thorina.—It is necessary for the mixture to be in the state of nitrate. We therefore dissolve the oxalates in nitric acid; although the pure oxalate of thorium is insoluble, the solution is easily made when the mixture contains 50 per cent of cerium. If the proportion of thorium present is greater, the oxalates must be decomposed by soda; in the presence of ThO, oxalate of cerium, which is attacked with difficulty when by itself, is easily decomposed in the cold. The solution of the nitrates, which should not contain much more than 0·5 of oxides, especially if thorina predominates, is evaporated to dryness or neutralised with ammonia; the residue is dissolved in water, and 10 c.c. of *distilled* peroxide of hydrogen (at 10 volumes) is added; it is then heated for a few moments to about 60°. The very voluminous precipitate is collected on a filter and washed, until the wash-waters are no longer precipitated by ammonia. It contains practically all the thorina, and the filtrate contains all the cerium within a few hundredths. It is therefore necessary to treat both fractions a second time. For this purpose the cerium is precipitated with ammonia; the precipitate must be dissolved on the filter by means of a few c.c. of dilute HNO_3, which are run through several times; the acid should be first warmed. The solution is evaporated to dryness, and, as before, treated with peroxide of hydrogen. The small quantity of thorina thus obtained is added to the first precipitate; the cerium remaining in solution this time is perfectly pure; it can now be precipitated by ammonia, calcined, and weighed in the state of Ce_3O_4. The second treatment of the peroxide of thorium is much more simple. The precipitate cannot be dissolved on the filter, as the disengagement of oxygen would cause a slight loss owing to the tiny drops of liquid which would be thrown out by the bubbles of gas. It must be removed from the filter, as carefully as possible, by means of a glass rod—this is not a difficult operation, thanks to the gelatinous nature of the precipitate; it is then dissolved in 2 c.c. of HCl, to which 2 c.c. of water and 1 grm. of HNO_3 have been added; the reduction is instantaneous. The solution is then passed through the filter to dissolve any of the material which may still adhere to it. The filter is then washed quickly, and the solution precipitated with ammonia. The hydroxide is collected on the same filter, dissolved in HNO_3, and the solution, neutralised with ammonia, is precipitated with peroxide of hydrogen. The same filters will easily serve for all the operations, the one for the oxide of cerium, the other for the thorina.

The peroxide of thorium, which has been twice precipitated by peroxide of hydrogen, contains only insignificant quantites of cerium (about 0·1 per cent); this is quite sufficient for ordinary analyses. Unfortunately the $Th_4O_7N_2O_5$ collected cannot be calcined; it decrepitates

* From the *Bull. Soc. Chim.*, Series 3, vol. xix.—xx., No. 6.

very strongly at a high temperature, being transformed into an impalpable powder which cannot be kept in the crucible; this causes a loss of at least 10 per cent. It is therefore necessary to once more reduce it, by a mixture of HCl and INH_4, precipitate by ammonia, and calcine to the state of hydroxide. All these operations, which appear to be very lengthy, do not really take up much time, thanks to the fact that most of the precipitates do not need any washing, for the reason that no matter is introduced which cannot be eliminated by calcination. We have given a few examples, showing the satisfactory nature of the results obtained by this method:—

		Taken.		Found.
1.	ThO..	0·3670		0·3655
	Ce_3O_4	0·0221		0·0229
2.	ThO..	0·3645		0·3640
	Ce_3O_4	0·0214	0·0354	0·0370
	LaO+DiO ..	0·0140		

In the two following analyses the cerium was only precipitated once, and therefore contained a little thorium:—

		Taken.	Found.
3.	ThO..	0·0508	0·0475
	Ce_3O_4	0·9485	0·9515
4.	ThO..	0·3651	0·3651
	Ce_3O_4	0·0207	0·0238

Mr. Dennis (*Zeit. Anal. Chem.*, xiii., p. 412, 1897) has proposed a very interesting reaction for the separation of thorium and cerium. He precipitates the neutral solution of the nitrates by the potassic salt of hydronitric acid, and then boils for a few minutes.

The thorina is thus precipitated integrally in the form of hydroxide, which can be immediately calcined. The only inconvenience of this process, which is as simple as it is charming, is the *total* precipitation of the thorina, as this same thorina will carry with it some small quantity of cerium which cannot be removed by subsequent precipitations. It is easy to make certain of this by treating one of the solutions used in the manufacture of Auer mantles, by KN_3; they contain from 1 to 1·5 per cent of cerium. The whole is precipitated by this means, and the filtrate does not contain any cerium. For the purpose of comparing the two methods, we took a synthetic mixture containing 0·0952 of ThO and 0·0927 of CeO.

After precipitation by KN_3, we found in the filtered solution 0·0896 of CeO quite free from thorium.

The thorina was re-dissolved in HNO_3, and precipitated by peroxide of hydrogen; the filtered solution then gave 0·0028 of CeO.

The thorina thus carried with it 3·34 per cent of cerium which was recovered by means of peroxide of hydrogen.

The method we propose is therefore much more accurate than that suggested by Mr. Dennis.

THE ESTIMATION OF MANGANESE AS THE SULPHATE AND AS THE OXIDE.*

By F. A. GOOCH and MARTHA AUSTIN.

The estimation of manganese by the conversion of salts of that element with volatile acids to the form of the anhydrous sulphate by the action of an excess of sulphuric acid, evaporation, and gentle heating, was formerly a recognised procedure. On the authority of Rose (*Ann. Phys. Chem.*, cx., 125), however, this method was set aside on account of the supposed difficulty of removing the excess of acid without disturbing the composition of the normal salt. Thus, Oesten, working under Rose's direction, obtained, upon submitting the crystalline hydrous sulphate $MnSO_4.5H_2O$ to heat, results which may be summarised and compared with the results obtained by Rose's sulphide method (the ignition of the residue with sulphur in hydrogen) as given in Table I.

The residues remaining after the gentle ignition of the sulphate weighed apparently several m.grms. more than should have been the case if the salt had been reduced to the normal anhydrous sulphate. At higher temperatures the sulphate turned brown and lost altogether too much weight. A comparison of the errors of the process in which the ignition was at low temperature with those of the sulphide process would seem to justify Rose's rejection of the former method for the latter. Upon re-calculating these results, however, using atomic weight in use at present—viz., Mn=55, S=32·06, O=16—it becomes plain that the errors of the two processes, as shown in Oesten's work, are not very different numerically, though with opposite signs (Table II.).

The most uncertain element in these experiments is the difficulty, well-recognised at present, of getting the hydrous manganous sulphate, upon which the experiments were made, in a perfectly definite condition of hydration.

Volhard (*Ann. d. Chem.*, cxcviii., 328) subsequently studied the sulphate process, and showed that manganous sulphate may be dehydrated, separated from an excess of sulphuric acid, and brought into definite condition for weighing as the anhydrous salt by careful and protracted heating over a special device of his own—a ring burner enclosed in a sheet-iron casing. Thus, on evaporating and dehydrating a solution of pure neutral manganous sulphate, Volhard obtained the results recorded in the following statement:—

Residue of $MnSO_4$ left by evaporation and dehydration	0·1635
Residue after treatment with three drops of H_2SO_4 and heating three hours ..	0·1635
Residue after heating two hours	0·1638
Residue after treatment with four drops of H_2SO_4 and heating two and a half hours	0·1635
Residue after heating three hours	0·1635

Similar results were obtained on evaporating with sulphuric acid and igniting in like manner an aqueous solution of manganous chloride. Volhard's recommendation of the method has not secured for it the acceptance which its simplicity and exactness would seem to demand—possibly because the periods of ignition appear to be considerable, and the manner of heating special.

In our own experiments with the sulphate process we have found that special apparatus is unnecessary, that the time of treatment may be short, and that the process is in every respect simple as well as very exact. We took for a starting-point manganous chloride prepared in the manner to be detailed. An aqueous solution of the so-called pure manganous chloride of commerce was boiled with pure manganous carbonate (to throw out aluminum, iron, and chromium), filtered, and precipitated with ammonium sulphide. The precipitate thus obtained was dissolved in a very slight excess of hydrochloric acid (to leave behind possible traces of nickel, cobalt, and copper), the solution was boiled to expel hydrogen sulphide, and precipitated with sodium carbonate. The manganous carbonate thus thrown down was boiled repeatedly with successive portions of water, and washed until the washings were free from chloride. The greater part of this purified carbonate was dissolved in the least possible amount of pure hydrochloric acid, the reserved portion of the carbonate was added, the mixture was boiled, and the solution of the purified and neutral manganous chloride was filtered from the excess of undissolved carbonate. Definite portions of this solution were precipitated with silver nitrate, and from the weight of the silver chloride thus obtained the amount of manganous chloride present was calculated. Portions of the solution thus standardised

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. v., p. 209.

Table I.

$MnSO_4.5H_2O$ taken. Grm.	$MnSO_4$ found. Grm.	Theory. Grm.	Error. Grm.	MnS found. Grm.	Theory. Grm.	Error. Grm.
1·659	1·043 (*a*)	1·037	0·006+	0·597	0·595	0·002+
	1·023 (*b*)		0·014−			
1·481	0·934 (*a*)	0·926	0·008+			
	0·905 (*b*)		0·021−			
	0·725 (*c*)		0·201−			
1·430	0·880 (*b*)	0·893	0·013−	0·509	0·512	0·003−

(*a*) Ignited gently. (*b*) Ignited at low red heat. (*c*) Ignited at strong red heat.

Table II.

$MnSO_4.5H_2O$ taken. Grm.	$MnSO_4$ found. Grm.	Theory. Grm.	Error. Grm.	MnS found. Grm.	Theory. Grm.	Error. Grm.
1·659	1·043	1·039	0·004+	0·597	0·599	0·002−
1·481	0·934	0·928	0·006+			
1·430				0·509	0·516	0·007−

Table III.

$MnSO_4$ calculated from AgCl found in 50 c.m.³ of solution A. Grm.	$MnSO_4$ found by treatment of 50 c.m.³ of solution A with H_2SO_4. Grm.	$MnSO_4$ found by treatment of 50 c.m.³ of various solutions with H_2SO_4.				
A.	A.	B.	C.	D.	E.	F.	G.
1. 0·3518	1. 0·3513	1. 0·3100	1. 0·3256	1. 0·3534	1. 0·3524	1. 0·3355	1. 0·5475
2. 0·3512	2. 0·3514	2. 0·3104	2. 0·3254	2. 0·3543	2. 0·3520	2. 0·3357	2. 0·5476
	3. 0·3518	3. 0·3096					

were drawn, for our experiments, from a burette into a weighed platinum crucible, sulphuric acid was added in amount more than equivalent to the manganese, the solution was evaporated on the water-bath until the water was removed, and then, supported by means of a porcelain ring or triangle, within a larger porcelain crucible used as a radiator, so that the bottom and walls of one were distant from the bottom and walls of the other by an interval of about 1 c.m., the crucible was heated more strongly. The outer porcelain crucible may be heated over a good Bunsen flame to a red heat without risk of over-heating the manganese sulphate within the inner crucible, and the ignition may proceed as rapidly as is consistent with the avoidance of mechanical loss by spattering. The results obtained by treatment of equal portions (50 c.m.³) of the same solution are given, together with the results of standardising the solution by precipitation with silver nitrate, in columns A (Table III.). In the other columns are given comparative results got in the treatment of equal portions of several other solutions employed subsequently in other work.

These results show plainly that the process of estimating manganese in the form of the anhydrous sulphate is both simple and accurate.

The estimation of manganese as the manganoso-manganic oxide, Mn_3O_4, has been so frequently criticised unfavourably that the method may be said to have passed from very general use, excepting in certain cases in which the directness of the process is a temptation to incur the risk of some uncertainty. The production of the other oxides of manganese in definite condition is thought to be even more uncertain. Manganese dioxide, MnO_2, begins, as Wright and Menke have shown (*Journ. Chem. Soc.*, xxx., 775) to lose oxygen at a temperature (about 210° C.) to which the hydrated oxide must be heated to free it from water, or very nearly that at which the nitrate is converted into the dioxide; so that the chance of producing an undecomposed dioxide by the ignition of the hydrated dioxide (the form in which the dioxide generally appears in analytical processes), or of the nitrate, is small. Manganic oxide, Mn_2O_3, is produced, it is said, from the other oxides by ignition at a low red heat under the ordinary conditions. The manganoso-manganic oxide, Mn_3O_4, forms, presumably, when an oxide of manganese is submitted, under ordinary atmospheric conditions, to the high heat of the blast-lamp. If the proportion of oxygen in the surrounding atmosphere is reduced below the normal, the conversion of Mn_2O_3 to Mn_3O_4 goes on very easily, as Dittmar has shown (*Journ. Chem. Soc.*, xvii., 294), at a temperature between the melting points of silver and aluminum, while if the proportion of oxygen in the surrounding atmosphere falls much below the normal, the reverse change, from Mn_3O_4 to Mn_2O_3, tends to take place at the same temperature. It is not surprising, in view of these phenomena, that the estimation of manganese as the oxide Mn_3O_4 should have fallen into disrepute; and yet, if the condition most favourable to the production of that oxide—a low proportion of oxygen in the surrounding air—can be maintained during the ignition, it is not impossible that the indications of the process might prove to be, under the conditions, reasonably accurate. Now, this may be exactly the condition of affairs when the ignition takes place ordinarily; for if the products of combustion displace the ordinary air about the crucible, the proportion of oxygen about the oxide falls to a low limit. We have made the experiment of enclosing the ignited crucible within an inverted crucible, so that the products of combustion should be held immediately about and above the ignited oxide, but our experience has shown that the object in view is attained, apparently, quite as well when the ignition is so arranged that the crucible simply rests well within the upper part of the flame of a strong Bunsen burner, or blast-lamp, in such manner that an oxidising flame covers nearly the entire wall of the crucible.

In the following experiments we have put to the test this matter of getting definitely the different oxides of manganese. We started with a known amount of pure anhydrous sulphate, prepared from the pure chloride in the manner previously described. This sulphate was converted by ignition into the oxide—presumably the oxide Mn_3O_4—the containing crucible being well within the upper flame of a powerful burner.

In the next step, this oxide was further oxidised by moistening it with nitric acid and heating the residue gently until the evolution of fumes ceased, the containing crucible being placed well above a porcelain crucible used as a radiator and heated so that only the bottom showed

a faint red heat. In this process the attempt was made to arrest the ignition at the point where the anhydrous dioxide was produced. As the table shows, and as would be expected, this attempt was only occasionally and partly successful.

The residue of the last process was then submitted to a higher heat. The platinum crucible containing the oxide was placed within and touching the bottom of a larger porcelain crucible which was heated to redness. Under these conditions the temperature should not be too hot, and the products of combustion should naturally be thrown so far away from the oxide undergoing ignition that circumstances should be favourable for the formation of the oxide Mn_2O_3. The event proved that the attainment of the exact condition corresponding to the symbol Mn_2O_3 is a matter of some uncertainty.

Next, the oxide was subjected to the highest heat of a strong Bunsen burner (or in some cases, the broad flame of a blast lamp), the crucible being well surrounded by the products of combustion. The results of this treatment, it will be seen, agree, with a single exception out of ten experiments, reasonably well with the theory for Mn_3O_4. By treating the final oxide with nitric acid and repeating the cycle of operations described, the observations of the phenomena were multiplied, until finally, the oxide formed last was treated with sulphuric acid, ignited in the manner previously detailed, and weighed as the anhydrous sulphate, thus showing that no significant loss of material had taken place in the series of manipulations. Table IV. comprises the results of these experiments. The Roman numerals indicate the order of treatment.

The inference is plain that the estimation of the manganese in the form of the manganoso-manganic oxide, Mn_3O_4, is by no means to be considered utterly untrustworthy when the process is conducted in the manner described, though it must be recognised that an irregular result way occur occasionally. The danger of accepting such an irregularity as a correct indication may be eliminated to a very considerable extent if the precaution is taken invariably to moisten the ignited oxide with nitric acid, and ignite again. The indications of harmonious results thus got may be taken with a fair degree of confidence. However, it is, in our judgment, by far the wiser and simpler plan to convert an oxide of manganese obtained in course of analysis into the sulphate and to weigh the manganese in that form.

TABLE IV.

$MnSO_4$ taken. Grm.		MnO_2.				Mn_2O_3.				Mn_3O_4.				$MnSO_4$.	
		Found. Grm.	Theory. Grm.	Error. Grm.		Found. Grm.	Theory. Grm.	Error. Grm.		Found. Grm.	Theory. Grm.	Error. Grm.		Found. Grm.	Error. Grm.
0·3712	II.	0·2114	0·2138	0·0024 −	III.	0·1975	0·1954	0·0021 +	I.	0·1880	0·1876	0·0004 +			
..	IV.	0·2137		0·0001 −	V.	0·1959		0·0005 +							
..	VI.	0·2147		0·0009 +	IX.	0·1986		0·0032 +							
..	VII.	0·2147		0·0009 +	X.	0·1957		0·0003 +	XI.	0·1881		0·0005 +			
..	VIII.	0·2138		0·0000 ±											
..	XII.	0·2145		0·0007 +	XIII.	0·1948		0·0006 −	XIV.	0·1877		0·0001 +			
..	XV.	0·2115		0·0023 −	XVI.	0·1939		0·0015 −	XVII.	0·1872		0·0004 −			
..	XVIII.	0·2158		0·0020 +	XIX.	0·1942		0·0012 −	XX.	0·1899		0·0023 +	XXI.	0·3709	0·0003 −
0·6436	..	..	..	..	..	..	..	..	I.	0·3247	0·3252	0·0005 −			
..	II.	..	..	..	..	..	..	..							
..	III.	0·3443	0·3707	0·0264 −	IV.	0·3372	0·3387	0·0015 −	V.	0·3245		0·0007 −			
..	VI.	0·3704		0·0003 −	VII.	0·3367		0·0020 −	VIII.	0·3244		0·0008 −			
..	IX.	0·3705		0·0002 −											
..	X.	0·3597		0·0110 −	XI.	0·3369		0·0018 −	XII.	0·3243		0·0009 −			
..	XIII.	0·3719		0·0012 +	XIV.	0·3362		0·0025 −	XV.	0·3244		0·0008 −	XVIII.	0·6432	0·0004 −
..	XVI.	0·3729		0·0022 +	XVII.	0·3366		0·0021 −					XIX.	0·6432	0·0004 −
..	..	0·3690		0·0017 −	..	..		..	..	..		..	XX.	0·6437	0·0001 +

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 19th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. T. M. Lowry, H. St. John, and J. Heaton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of favour of Messrs. John Brighouse Buchan, 17, Steven Street, Stretford, Manchester; Charles William Tisdale Davies, Wye, Kent; Robert Findlay Hislop, Craigielea, Paisley; George Herbert Martin, New College, Eastbourne; Charles James Meads, Brooklyn, Erlanger Road, St. Catherine's Park, S.E.; Matthew Joseph Sheridan, 20, Heathland Road, Stoke Newington, N.

The following papers were read:—

79. "*The Liquefaction of Hydrogen and Helium.*" By James Dewar, LL.D., F.R.S.

In a paper entitled "The Liquefaction of Air and Research at Low Temperatures" (*Proc.*, 1895, xi., 221), an account was given of the history of the hydrogen

problem and the result of the author's experiments to the end of the year 1895. The subject was again discussed in a Lecture on "New Researches on Liquid Air" (*Proc. Roy. Inst.*, 1896, xv., i., 144), and a sketch given of the apparatus employed for the production of a jet of hydrogen containing liquid. It was shown that such a jet could be used to cool substances below the temperature which could be reached by the use of liquid air, but all attempts to collect the liquid in vacuum vessels failed. The type of apparatus used in these experiments worked well, so it was resolved to construct a much larger liquid air plant, and to combine with it circuits and arrangements for the liquefaction of hydrogen. This apparatus, admirably constructed by the engineers, Messrs. Lennox, Reynolds, and Fyfe, took a year to build up, and many months were occupied in testing and making preliminary trials. The many failures and defeats need not be detailed.

On May 10th hydrogen was liquefied by allowing the gas, cooled to $-205°$, and under a pressure of 180 atmospheres, to escape continuously at the rate of from 10 to 15 cubic feet per minute from the nozzle of a coil of pipe in a double silvered vacuum vessel of special construction surrounded with a space kept below $-200°$. Liquid hydrogen commenced to drop from this vacuum vessel into another doubly isolated by being surrounded with a third. On this occasion 20 c.c. of liquid hydrogen were collected in about five minutes, and on May 12th 50 c.c. were obtained before the hydrogen jet froze up from the solidification of air in the pipes. The yield of liquid was about 1 per cent of the gas. The hydrogen in the liquid condition is clear and colourless, showing no absorption spectrum, and the meniscus is as well defined as in the case of liquid air. The liquid must have a relatively high refractive index and dispersion, and the density appears to be in excess of the theoretical value, 0·18 to 0·12, deduced respectively from the atomic volume of organic compounds and from the limiting density found by Amagat for hydrogen gas under infinite compression. The author's experiments on the density of hydrogen in palladium gave a value 0·62 for the substance in combination, and it will be interesting to find the density of the actual liquid at its boiling-point. Not having arrangements at hand to determine the boiling-point, two experiments were made to prove the excessively low temperaturs of the boiling fluid. In the first place, a long piece of glass tubing, sealed at one end, but open to the air at the other, and cooled by immersing the closed end in liquid hydrogen, immediately filled, where it was cooled, with solid air. The second experiment was made with a tube containing helium.

The *Bulletin* of the Cracow Academy for 1896 contains a paper by Professor Olszewski, entitled "A Research on the Liquefaction of Helium," in which he states that "As far as my experiments go, helium remains a permanent gas, and apparently is much more difficult to liquefy than hydrogen." Helium which had been extracted from Bath gas by the liquefaction method described last year (*Proc.*, 1897, xiii., 190), and sealed up in a bulb with a narrow tube attached, was placed in liquid hydrogen, and a distinct liquid was seen to condense. A similar experiment made with the same helium tube in liquid air under exhaustion instead of in liquid hydrogen gave no visible condensation. It would thus appear, as already suggested by the author (*loc. cit.*), that there cannot be any great difference in the boiling-points of helium and hydrogen. A fuller account of the work will appear in the *Transactions*.

All known gases have now been condensed into liquids which can be manipulated at their boiling-points under atmospheric pressure in suitably arranged vacuum vessels. With hydrogen as a cooling agent, it will be possible to get within 20° or 30° of the zero of absolute temperature, and its use will open up an entirely new field of scientific inquiry.

During the whole course of the low temperature work carried out at the Royal Institution, the invaluable aid of Mr. Robert Lennox has been at the author's disposal, and it is not too much to say that, but for his engineering skill, manipulative ability, and loyal perseverance, the present successful issue might have been indefinitely delayed. The author's thanks are also due to Mr. J. W. Heath for valuable assistance in the conduct of these experiments.

Discussion.

Sir William Crookes proposed that the Fellows of the Society should offer their best congratulations to the President on the striking success which had attended his remarkable attempt to liquefy the last of the "permanent" gases—hydrogen and helium.

Dr. Armstrong, in seconding the proposal, said that in the future the fact that the liquefaction of hydrogen had been achieved by a President of the Society would no doubt be recalled with interest. In early days, the discussion of the properties of hydrogen had attracted much attention in the Society, when Sir Benjamin Brodie advocated the view that it must be supposed to have metallic properties, a view subsequently strongly supported by Graham's discovery of hydrogenised palladium. He ventured to think, however, that the subject had been regarded too much from the inorganic side, and that when the evidence to be derived from organic chemistry was taken into account it was more probable that hydrogen would be found to resemble the petroleum hydrocarbons rather than the metals.

He then asked whether the President's statement that argon solidified when cooled in liquid air did not preclude the presence of argon in the helium from Bath gas, which gave only a liquid when cooled in hydrogen.

The motion was carried by acclamation.

The President, in acknowledging the compliment, said that the facts referred to by Dr. Armstrong proved that the helium employed in the liquefaction experiments did not contain argon. It was possible that hydrogen might be present in small quantity, but otherwise the helium was pure.

80. "*The Action of Formaldehyde on Amines of the Naphthalene Series.*" (Part I.). By Gilbert T. Morgan, B.Sc.

By the interaction of methylal, acetone, and β-naphthylamine, Reed (*J. Prakt. Chem.*, 1887, xxxv., 314) obtained naphthacridine, $C_{21}H_{13}N$ (m. p. 216°) and a substance melting at 202—203°, to which he gave the formula $C_{24}H_{20}N_2$.

The author finds that when formaldehyde (40 per cent solution) acts on β naphthylamine in alcoholic solution in the presence of hydrochloric acid, four basic substances are produced. Two of these have the composition corresponding with the formula $C_{21}H_{13}N$; one crystallises in orange needles melting at 225—226°, and the other in straw-coloured needles melting at 216°. The latter was found to be identical with naphthacridine.

The third substance crystallises in colourless prisms often showing cruciform twinning, melts at 203°, and is identical with the compound of this melting-point described by Reed. Its composition is expressed by the formula $C_{23}H_{18}N_2$, and, as the author has obtained it by the action of formaldehyde alone on β-naphthylamine, it follows that acetone plays no part in the condensation.

The fourth compound is obtained only in small quantity, crystallises in silky needles having a faintly yellow tinge, melts at 186—187°, and has the formula $C_{22}H_{16}N_2$. Its *hydrochloride*, $C_{22}H_{16}N_2,HCl$, and *nitrite*, $C_{22}H_{16}N_2,HNO_2$, have been prepared, and the base can be regenerated from either salt by means of aqueous alkalis.

The orange-coloured base melting at 225—226° stands in very close relationship to the isomeric naphthacridine (m. p. 216°), and is converted into it both easily and quantitatively. Its behaviour with hydrogen chloride is remarkable. When it is triturated with concentrated

hydrochloric acid, or submitted to the action of the dry gas, it forms a green hydrochloride, from which the orange base is obtained; but when dry hydrogen chloride is passed into its solution in benzene or in glacial acetic acid, a yellow hydrochloride is produced, which yields naphthacridine (m. p. 216°). The orange base is probably a labile form of naphthacridine. Methods for preparing each form in quantity are given in the paper, and the *hydriodide*, *methiodide*, and *ethiodide* of naphthacridine (m. p. 216°) are described.

The products of the interaction between formaldehyde and α-naphthylamine have been examined with results which will be communicated in a subsequent paper, and the invstigation is being extended to derivatives of both α- and β-naphthylamine.

Discussion.

Prof. Dunstan pointed out that commercial formalin usually contains acetone, so that, unless the author had satisfied himself of the purity of the formaldehyde, the fact that the interaction of the commercial solution and β-naphthylamine gave rise to the condensation product did not necessarily tell in favour of the view that acetone was not concerned in the action.

Mr. Morgan, in reply, said that the formaldehyde solution employed could have contained only a small amount of acetone. The base melting at 203° is readily reduced to naphthacridine by means of hydriodic acid and phosphorus, and this fact not only supports the formula adopted by the author, but also—taken in conjunction with the large yield of the base when prepared from β-naphthylamine and formaldehyde—makes it improbable that acetone takes any part in the condensation.

81. "*On the Constitution of Oleic Acid and its Derivatives.*" (Part I.). By Frank George Edmed, B.Sc.

Oleic and elaidic acids, when oxidised by weak alkaline permanganate, yield two dihydroxystearic acids, melting respectively at 134° and 99° (Saytzeff, *J. Russ. Chem. Soc.*, 1885, xvii., 417). The author finds that, while these acids are the chief products of the reaction, pelargonic, azelaic, and oxalic acids are also formed at the same time. These acids result from the continued action of the oxidising agent on the dihydroxystearic acids, and no evidence could be obtained of the formation of sebacic, suberic, and caprylic acids, which, with azelaic acid, have been stated to be the products of the further action of permanganate (Spiridonoff, (*J. Russ. Chem. Soc.*, 1887, xix., 646). The dihydroxystearic acid obtained from elaidic acid is much more easily oxidised than its isomeride, a fact which is consistent with the stereoisomeric formula ascribed to elaidic acid. The formation of pelargonic and azelaic acids affords additional evidence in support of the formula $CH_3(CH_2)_7CH{:}CH(CH_2)_7CO_2H$, for both oleic and elaidic acids.

Oleic acid was also oxidised with a weak solution of chromic acid; the action was very slow, and a considerable quantity of azelaic acid, but only a trace of pelargonic acid, was obtained. No other products could be isolated, and the action appears to be similar to that of the permanganate.

The products resulting from the fusion of oleic and of elaidic acids with potash were quantitatively examined, and it was found in both cases that the yield of palmitic acid was approximately theoretical, but that the quantity of acetic acid was extremely small. Oxalic acid was also produced in the reaction, and the amount exceeded that of the acetic acid, but neither pelargonic nor azelaic acids could be detected, nor could any dihydroxystearic acid be recognised, although from Wagner's explanation of the reaction (*Ber.*, 1888, xxi., 3353) this might be expected to be an intermediate product.

Discussion.

Mr. Hehner was by no means convinced that the double linkage occurred between the central carbon atoms in the oleic acid formula. No doubt oleic acid on oxidation formed azelaic acid by preference, but as by other means—for instance, by treatment with sulphuric acid or zinc chloride—lactones were very readily obtained, it seemed possible that oleic acid was a labile compound, and that the double linkage had not a definite position in the molecule. He was astonished at the excellent yield of dihydroxystearic acid obtained by the author by means of alkaline permanganate; in the most favourable circumstances he had been able to obtain only about 40 per cent of the theoretical yield, and this, he thought, was also the experience of other workers. The oxidation by means of chromic acid might have succeeded better if a solution of chromic anhydride in acetic acid had been employed instead of a mixture of bichromate and sulphuric acid. As to the deficiency in the yield of acetic acid in the potash fusion, might not some of the acetate have decomposed into methane?

The question arose whether oleic acid could be regarded as a single substance. The number of isomerides possible in the case of compounds containing 18 carbon atoms was enormous, and, while many were well known among the lower members of the series, it was remarkable that when a chain of about 10 carbon atoms was reached, all reference to isomerides disappeared from the text-books, solely, in his opinion, because means for their separation had not been devised. At the same time indications existed—such as slight differences in the optical behaviour of oils of a similar degree of unsaturation, and in the solidifying points of the fatty acids separated from them—which pointed towards isomerism. It was essential to elucidate this point before studying the constitution of the substance called oleic acid, especially as most of the work which had been done was antecedent to the recognition of the existence of less saturated acids, such as linolic and linolenic acids and their homologues, which were almost invariably present with acids of the oleic class.

Dr. Crossley was surprised to learn that a nearly theoretical yield of dihydroxystearic acid was obtained by oxidising oleic acid with permanganate, as in similar experiments he had never succeeded in obtaining more than 40 per cent of the amount theoretically possible. Referring to Wagner's explanation of the production of palmitic from oleic acid by fusion with potash, he pointed out that it received support from many cases in which this alkali seems to act simultaneously as an oxidising and reducing agent, and suggested that the fusion of oleic acid with soda might lead to interesting results, as caustic soda apparently does not exercise a reducing action.

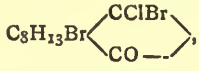
Prof. Tilden said that, in his opinion, a body of evidence had been brought forward which amounted almost to positive proof of the correctness of the symmetrical formula for oleic acid. And, referring to the remarks of Mr. Hehner, he would venture to say that if it came to a question of the credibility of evidence, he should distinctly prefer the testimony derived from the action of a 1 or 2 per cent solution of permanganate in the cold to that of such agents as zinc chloride or caustic potash, which required a high temperature.

Prof. Dunstan doubted whether there was any real evidence that crystallisable oleic acid obtained from different oils is not a single substance. He thought it more probable that the differences Mr. Hehner had alluded to were due to impurities occurring in the natural oils.

Mr. Edmed, in reply, said that the quantitative yield of palmitic acid in the potash fusion precluded the supposition that the oleic acid employed contained a branched-chain isomeride. It was not possible to accept Mr. Hehner's suggestion that the small amount of acetic acid obtained was due to a decomposition of potassium acetate into methane during the reaction, as the temperature was not allowed to exceed 230° during the fusion.

82. "*Stereoisomeric Derivatives of Camphor.*" By T. M. Lowry, B.Sc.

In addition to the case of stereoisomerism referred to in a previous note (*Proc.*, 1897, xiii., 159), the author has investigated that of the dibromochlorocamphors,—



obtained by heating chlorocamphor with an excess of bromine in sealed tubes. When re-crystallised five times, the product melted at 81° and had a specific rotatory power $[\alpha]_D = 44{\cdot}5°$ in a 5 per cent solution in chloroform; after five more crystallisations, the rotatory power was raised to 51·3°, but no increase was observed after sixteen further crystallisations. The melting-point also was constant at 84°. There can be no doubt that the change in rotatory power indicates the presence of two stereo-isomerides, and the product must, therefore, be an isomorphous mixture similar to that afforded by the bromo-chlorocamphors previously described, from which it differs only by the presence of an additional bromine atom in the β-position.

PHYSICAL SOCIETY.

Ordinary Meeting, May 27th, 1898.

Mr. Shelford Bidwell, President, in the Chair.

A paper by Messrs. Edwin Edser and C. P. Butler on "*A Simple Method of Reducing Prismatic Spectra*," was read by Mr. Edser.

The production of interference-bands in a continuous spectrum is capable of furnishing a reference-spectrum which can be employed to determine the wave-lengths corresponding to the bright lines in a spectrum of a metal or of a gas. The authors discuss various methods by which such bands can be formed. In their final experiments, an air-film between two plane parallel glass plates is inserted in front of the slit of the spectrometer, in the path of the incident light. Owing to the interference of the direct ray with that twice internally reflected, bright bands separated by dark intervals are observed in the spectrum; these bright bands correspond to a series of different waves, whose lengths are easily determined for the whole series, when two of them are known. The bands are much improved by partial silvering of the two internal surfaces of the glass. It has been found that ordinary plate-glass, if well chosen, is good enough for all these experiments. In order to adjust for parallelism, a spot of light, or the filament of a glow-lamp, is viewed through the silvered surfaces. A long train of images is generally visible; these must be brought into coincidence. If now a sodium flame is looked at through the film, interference bands are seen. These bands must be adjusted by pressure, to be as broad as possible. An arc-lamp is used for illuminating the collimator slit. The authors exhibited the apparatus, and showed photographs of spectra-scales, with the appropriate wave-lengths calibrated upon them by this method. The results obtained were read from the spectrometer to 0·4 of a tenth-metre with an ordinary pocket lens. A simple graphic method enables wave-lengths, corresponding to a great number of spectral lines, easily to be determined by inspection. The phase-changes introduced by the silver do not affect the final result.

Prof. Threlfall congratulated the authors on their discovery of a method that would greatly reduce the labour of calibrating spectra, and at the same time give such accurate results.

Prof. Boys said the simplicity of the apparatus added greatly to the value of the method. It would seem to him better if the slit were somehow contrived within the film-space. All want of definition due to rays falling at different angles upon the collimator object-glass would thus be avoided, and only a small part of the glass plates, *i.e.*, the slit, would require to be strictly parallel planes. The limit of accuracy in the authors' method depended upon the collimator, not upon the optical perfection of the silvering of the plates.

Mr. Butler pointed out that previous methods had always required experienced spectroscopists for mapping out results. In the new method that work could easily be done by an assistant.

Mr. Edser said that, by putting the two plates immediately in front of the slit, only a very small part of the glass is concerned in the action; light coming through at an angle would not reach the lens in the collimator.

Prof. Boys, Vice-President, then took the chair, and

Mr. Campbell Swinton read a paper on "*Some further Experiments on the Circulation of the Residual Gaseous Matter in Crookes Tubes.*"

In the discussion that followed the former paper on this subject, at the Physical Society on March 25, 1898, Mr. Appleyard had suggested that, in tracing the cause of the rotation of the exploring mill, it would lead to simpler results if the vanes were made of some light conducting substance, for it was probable that mica introduced complications by retaining the charges. Prof. Boys then pointed out that the mica might be gilded. Such a tube has now been made by Mr. Wolff. With the gilded mica vanes so placed as to be outside the cathode stream, the mill behaves in a manner similar to the non-conducting insulated mill. It shows a greater tendency to assume a position of stability, due to electro-static induction; this renders it somewhat troublesome in starting, but when once under way, the mill rotates always when excited. Occasionally, when starting, a few reverse revolutions are observed. These are probably due to electro-static influence and momentum, and also possibly to eddy currents in the residual gaseous matter. But it is found, in all cases, that rotation in the direction that indicates a stream of residual gaseous matter from anode to cathode follows the reversal immediately after one or two oscillations. An electrometer connected to the mill through the pivot and needle-point, shows the vanes to be always electrified positively. The results are confirmed by a second tube with oblique vanes. The author concludes that at very high exhaustions there exists a molecular or atomic stream from anode to cathode, which carries a positive charge, and travels at high velocity outside the opposite cathode stream.

Mr. J. Quick asked what was the minimum degree of exhaustion required to produce these results.

Prof. Boys said that the experiment gave some amount of probability to the truth of Mr. Campbell Swinton's hypothesis, but it did not altogether prove the mechanical theory of rotation to be correct. He was glad that a chance suggestion at the last discussion had led to such interesting experiments being continued.

Prof. Threlfall mentioned that Boettger had devised a method for gilding mica, by a chemical process, that was much to be preferred to ordinary gilding.

Mr. Campbell Swinton said it was necessary to exhaust the tubes as completely as possible; to a point where it was only just possible for any discharge at all to pass through them. If the rotation was due to electrification, there must still be some mechanical process whereby the charges get to the vanes,—a stream of residual gas satisfied that condition.

The Vice-President proposed votes of thanks, and the meeting adjourned until June 10th.

Dinner of the Chemical Society.—In consequence of the death of Lord Playfair, the proposed dinner on June 9th, which was to be given by the Chemical Society to Lord Playfair and other Past Presidents who had been Fellows of the Society for fifty years, is postponed until the end of October. Dr. Mond's Garden Party on June 10th is also postponed.

DENSITY AND BOILING-POINT OF LIQUID HYDROGEN.

At the Chemical Society last night the President, Professor Dewar, gave an account of his latest researches on liquid hydrogen.

Two of its physical constants have now been determined. Its boiling-point in air is −238° C., or 35° absolute, determined by a platinum resistance thermometer; this value is higher by something like 17 per cent than the value obtained by Olszewski by adiabatic expansion. The whole range of liquid hydrogen is only about 50° from the absolute zero, because its critical point must be about 50° absolute. Thus it appears that there can only be a few degrees + or − in the different estimates based on theoretical conceptions as to its boiling-point. But these few degrees are really a large percentage of the whole, seeing that the range is so small. This value of the boiling-point enables us to predict with almost certainty that by no conceivable means at our present command shall we ever get nearer the absolute zero than −250° C., or, say, +20° absolute; that is, the practical fall in temperature that liquid hydrogen will give under high exhaustion will never exceed 10° or 15° lower than its present boiling-point.

The next physical constant that has been determined is the density of hydrogen. As already described, the substance appears as a transparent fluid, with a well-defined meniscus, and it easily drops from one vessel to another, and may be said to collect with considerable rapidity. The appearance of the liquid would suggest a density probably not unlike liquid marsh gas, which has a density of 0·41 at its boiling-point in air, and is the least dense liquid known under such conditions. On allowing 10 c.c. of liquid hydrogen to evaporate, collecting the gas, and measuring its volume, the approximate density can be accurately determined. The resulting value comes to be a number rather less than 0·07. The result is, the liquid is about one-fourteenth the density of water, or it bears the same relation to water that hydrogen gas bears to air. The atomic volume, therefore, of liquid hydrogen is about 14; the atomic volume of liquid oxygen being about 13·7. The atomic volumes, therefore, of hydrogen and oxygen at their respective boiling-points are very close to each other. The density of the vapour of hydrogen at its boiling-point, assuming no abnormal condensation, is about half that of air, or approaches that of marsh gas at the ordinary temperature. The ratio of the hydrogen vapour at its boiling-point to the liquid is as 1 to 100, whereas in the case of oxygen the similar ratio is as 1 to 255.

Liquid hydrogen is in all respects the most extraordinary fluid chemists have ever had to deal with. No chemist could have anticipated that a liquid with a density of one-fourteenth that of water could have been capable of collection and manipulation in vacuum vessels with the same ease, practically, as manipulation with liquid air was carried on ten years ago, and that by its means we shall approach within 20° to 25° of the absolute zero.

On the Ammoniacal Bromides of Silver.—M. Jarry.—When submitted to the action of liquefied ammonia gas, dry bromide of silver loses its yellow colour and is transformed into a white powder; the excess of liquid is evaporated off, keeping the temperature at −30°. If now the temperature be gradually raised, at about +4° an abundant disengagement of ammonia is observed, though the powder still remains white; towards +35° another disengagement of ammonia gas takes place, and this time the bromide returns to its original yellow colour.—*Comptes Rendus*, cxxvi., No. 16.

OBITUARY.

LORD PLAYFAIR.

It is with great regret that we record the death of the Right Hon. Lord Playfair, K.C.B., F.R.S., which took place at his residence in Onslow Gardens on Sunday last, from bronchitis.

Lord Playfair has long been a prominent figure in scientific circles; he was one of the oldest Fellows of the Chemical Society, and would have been the principal guest at a dinner which had been arranged for the 9th of this month to entertain him and six other Past Presidents of the Chemical Society, all of whom have been Fellows for at least fifty years.

Lord Playfair was the son of Mr. George Playfair, Chief Inspector-General of Hospitals of Bengal, and was born at Meerut, Bengal, on May 21st, 1819; he was therefore just 79 years of age. After leaving St. Andrews, N.B., where he passed his school-days, he went to study chemistry at the Andersonian University, Glasgow, under Prof. Graham. In 1838 he went to Giessen, and there studied organic chemistry under Liebig, several of whose works he translated into English. In 1843 he went to Manchester, where he was appointed Professor of Chemistry in the Royal Institution; and in 1844, on the recommendation of the late Sir Robert Peel, he was appointed on the Commission constituted to examine into the sanitary condition of our large towns and populous districts, after which he was appointed Chemist to the Museum of Practical Geology. At the close of the Great Exhibition of 1851 he was made a Companion of the Bath, in recognition of his services as Special Commissioner in charge of the department of Juries, which post he again filled in 1862. In 1853 he was appointed joint Secretary, with Mr. Henry Cole, of the Department of Science and Art, and in 1856 he became Chief Inspector-General of Government Museums and Schools of Science. In 1857 Lord Playfair was elected President of the Chemical Society, and in 1858 he became Professor of Chemistry at the University of Edinburgh, where he had the honour of numbering the Prince of Wales and Prince Alfred among his pupils. He was one of the Royal Commissioners on the Cattle Plague, and was Chairman of the Royal Commission on the Scottish Fisheries. In 1874 he produced an elaborate scheme for the reorganisation of the Civil Service. He entered Parliament in the Liberal interest for the University of Edinburgh and St. Andrews in 1868, and in 1873-74 he held office as Postmaster General. In 1880 he was appointed Deputy Speaker of the House of Commons, and was made a K.C.B. on his retirement from this office and from the Chairmanship of Ways and Means in 1883. Lord Playfair was a Privy Councillor of the Queen, and of the Prince of Wales in the Duchy of Cornwall. He was a member of many learned societies and had many foreign orders; he was raised to the Peerage in 1892.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 16, April 18, 1898.

General Reaction of the Ethenic Carbides. Corresponding Mercuric Compounds.—G. Denigès.—By acting on butylene with mercuric sulphate in acid solution, compounds may be obtained corresponding to the general formula—

$$(SO_4Hg.HgO)_3R'' = (SO_4 \begin{matrix} Hg \\ \diagup\diagdown \\ Hg \end{matrix} O)_3R''$$

in which R'' represents an ethenic carbide. These compounds of a yellow colour dissolve easily in hydrochloric acid, accompanied by effervescence when the carbide combined with the mercury is volatile at the working temperatures.

Heat of Formation of some Quinones of High Molecular Weights.—A. Valeur.—The heat of formation of several quinones, starting from the corresponding hydrocarbides, are:— Ordinary quinone +129·1 cals., toluquinone +118·5 cals., thymoquinone +137·9 cals., α-naphthoquinone +138·1 cals., β-naphthoquinone +131·5 cals., anthraquinone +159·1 cals., phenanthraquinone +152·4 cals., retenequinone +167·2.

Heat of Neutralisation of Ethyl-phosphoric Acid.—G. Belugou.—The quantity of heat given off by the second molecule of alkali acting on the acid ethers is greater than that produced by phosphoric acid under the same conditions; it appears, therefore, that the di-potassic mono-phosphate ethers are less easily dissociable in aqueous solution than are the corresponding phosphates. Ethyl-phosphoric acid behaves in the same way as phosphoric acid towards helianthine and phthalein, and can therefore be estimated volumetrically.

Journal de Pharmacie et de Chimie,
Series 6, vol. vii., No. 6.

The Assay of Bronze used for Coinage. — A. Riche. — Reprint from the *Comptes Rendus*. Already noticed in this column.

The Simultaneous Volumetric Estimation of Sulphuric Acid and Lime in Waters. — L. Robin. — Already inserted in full.

The Detection of Rocou in Milk.—A. Leys.—The artificial colouration of milk is extending, especially by the addition of certain materials which impart to it a faint yellow tinge. If a sample of milk is suspected of containing *rocou*, 50 c.c. are treated in a flask with double its volume of a mixture of alcohol at 93°, 2400 c.c., ether 3200 c.c., water 200 c.c., and ammonia at 0·92 density, 80 c.c. After being thoroughly shaken, the flask is left quiet for a time, and the contents separate into two layers. The lower one, which consists of the casein and similar bodies in ammoniacal ethero-alcoholic solution, contains also the *rocou*, which imparts to the liquor a greenish-yellow tinge. After waiting for about twenty minutes, this lower layer is separated, and treated with half its volume of a 10 per cent solution of sulphate of sodium, which must be added in small portions at a time, while the flask is kept constantly shaken; a voluminous white precipitate, which quickly rises to the surface, is formed. By this means the greater part of the casein is removed without interfering with the colouring matter, which still remains in solution; this can then be extracted by means of amylic alcohol. After further treatment, a strip of cotton, which has been placed in the solution during evaporation, will, if *rocou* is present, immediately take a pink colour, while in the opposite case it will be yellow, after being dipped in a solution of citric acid.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Society of Chemical Industry, 8. "Conditions existing in Acetylene Generators," by Prof. V. B. Lewes.
TUESDAY, 7th.—Royal Institution, 3. "Literary Criticism in Greece," by Professor S. H. Butcher, LL.D.
THURSDAY, 9th.—Royal Institution, 3. "Modern Methods and their Achievements in Bacteriology," by Edward E. Klein, M.D., F.R.S.
FRIDAY, 10th.—Royal Institution, 9. "Some Experiments with the Telephone," by The Right Hon. Lord Rayleigh, F.R.S., &c.
SATURDAY, 11th.—Royal Institution, 3. "The Temples and Ritual of Asklepios at Epidaurus and Athens," by Richard Caton, M.D., F.R.C.P.

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MASON UNIVERSITY COLLEGE, BIRMINGHAM.

FACULTY OF SCIENCE.

RESEARCH SCHOLARSHIPS.
(Founded by the late T. Aubrey Bowen, Esq., of Melbourne, Australia).

(*a*) Two BOWEN SCHOLARSHIPS in ENGINEERING, each of the value of about £96.
(*b*) One BOWEN SCHOLARSHIP in METALLURGY, of the value of about £96.
(*c*) Three PRIESTLEY SCHOLARSHIPS in CHEMISTRY, each of the value of about £96.

The object of these Scholarships is to encourage higher work and research in Scientific Professional Engineering and in Chemical and Metallurgical Science.
Applications, supported by details of educational training and references to former teachers and others, should be sent to the Registrar on or before the 11th June, 1898. The awards will be made in September next, and the Scholarships will be tenable during the Session 1898-9.
Further particulars may be obtained on application to the REGISTRAR.

PATENTS, DESIGNS, AND TRADE MARKS ACTS, 1883 TO 1888.

NOTICE IS HEREBY GIVEN, that JAMES YATE JOHNSON, of 47, Lincoln's Inn Fields, London, has applied for leave to amend the Specification of the Letters Patent No. 18221 of 1896, for "Improvements in the manufacture and production of phthalic and sulpho-phthalic acids."
Particulars of the proposed amendments were set forth in the Illustrated Official Journal (Patents) issued on the 25th May, 1898.
Any person or persons may give notice of opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

C. N. DALTON,
Comptroller General.
JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C.,
Agents for the Applicant.

TO SPIRIT DISTILLERS, BREWERS, MANUFACTURING CHEMISTS, AND OTHERS.

MESSRS. FULLER, HORSEY, SONS, & CASSELL are instructed to SELL by AUCTION, in lots, at the Distillery, 159, Blackfriars Road, S.E., on Tuesday, June 14, 1898, at 12 o'clock precisely, DISTILLING PLANT and MACHINERY, including a 585 gallon copper rectifying still, one 1623 and one 995 gallon copper pot stills, three copper worms, two circular cast-iron worm tubs, two copper spirit safes, copper piping and gun-metal cocks, copper boiling pan, set of three throw gun-metal pumps, three lift and force pumps, Cornish and vertical boilers, table engine, iron steam and water piping, 75 oak spirit vats and casks, copper measures, cranes, and utensils, two useful horses, four pair and single horse vans, harness, stable utensils, office furniture, and other effects. May be viewed the day preceding, and catalogues had on the premises; and of Messrs. Fuller, Horsey, Sons, & Cassell, 11, Billiter Square, E.C.

THE CHEMICAL NEWS.

Vol. LXXVII., No. 2011.

ON THE LINDO-GLADDING METHOD OF DETERMINING POTASH.

By A. L. WINTON,
Chemist, Conn. Agricultural Experiment Station, and Reporter on Methods of Potash Determination for the Association of Official Agricultural Chemists for the Years 1896 and 1897;
and
H. J. WHEELER,
Chemist, R. I. Agricultural Experiment Station, and Reporter on Methods of Potash Determination for the Association of Official Agricultural Chemists for the Years 1894 and 1895.

In view of certain criticisms of the Lindo-Gladding method of potash determination which have appeared of late, notably those by Vogel and Haefcke (*Die Landw. Versuch-Stationen*, 47, 1896, pp. 112—117), we were appointed a committee by the Association of Official Agricultural Chemists of the United States to prepare an article setting forth certain work bearing upon the points involved.

At the regular meeting of the Association in Washington in 1890, Breyer and Schweitzer (U.S. Dept. of Agric., Div. of Chem., *Bull.* 28, 1890, p. 73) called attention to certain comparative determinations made by them, which indicated that the use of sodium chloride was unnecessary. The mean difference in the results with and without sodium chloride amounted to but 0·04 of a per cent, and in but two cases out of fifty was the difference over 0·10 of a per cent. In 1891, Winton (U.S. Dept. of Agric., Div. of Chem., *Bull.* 31, 1891, pp. 148—150) investigated the matter thoroughly, and in tests conducted with commercial potash salts and twenty-four mixed fertilisers showed that the results with and without the addition of sodium chloride were practically identical (compare Fresenius, *Zeit. f. Analyt. Chem.*, xvi., p. 63). The same line of study was further pursued in 1892 by Payne (U.S. Dept. of Agric., Div. of Chem., *Bull.* 35, 1892, pp. 58—61), in co-operation with twenty-two chemists in seventeen different laboratories, working with a variety of substances. As a result of these investigations by the Association, the use of sodium chloride was discontinued (U.S. Dept. of Agriculture, Div. of Chem., *Bull.* 35, 1892, pp. 197—198). This was done, not because inaccurate results were obtained by its use, but in order to abbreviate the method by striking out a useless and cumbersome detail.

Notwithstanding the fact that it had already been abundantly shown that there was practically no difference in the results obtained with and without the use of sodium chloride, Breyer and Schweitzer (*Journ. of Anal. and Appl. Chem.*, vi., No. 8, 1892, p. 477) asserted that its use was a source of error. Their claim that it was unnecessary was merely a reiteration of what had already been shown by the work of the Association.

Aside from the undesirability of employing sodium chloride, the only unfavourable criticism of the Lindo-Gladding method worthy of note which has appeared, is based upon the assumption that a considerable error is introduced through double decomposition resulting from the contact of the ammonium chloride wash solution with potassium platinichloride. Breyer and Schweitzer (*Journ. of Analyt. and Appl. Chem.*, vi., No. 8, 1892, pp. 474—477) and N. Robinson (*Journ. Am. Chem. Soc.*, xvi., 1894, pp. 366, 367) mention errors thus arising, and the two former chemists claim that the amount of the same is considerable. Their conclusions in this respect are based chiefly upon the amount of potassium chloride said to have been recovered from the ammonium chloride wash solution which had already been employed in washing precipitates of potassium platinichloride. It does not appear, however, that blank determinations were made for the purpose of ascertaining the amount of potash, if any, contained in the ammonium carbonate, ammonium oxalate, and in the 7 grms. of barium hydrate and other reagents employed in the recovery of the potash. In view of the fact that considerable amounts of potash are frequently present in certain so-called chemically pure reagents employed in potash determinations (U.S. Dept. of Agriculture, Division of Chem., *Bull.* 43, 1894, pp. 21, 22; also *Bull.* 47, 1895, pp. 16, 17; and *Bull.* 49, 1896, pp. 30—32), it is obvious that a large part of the potash said by Breyer and Schweitzer to have been recovered from the wash solution may have been derived from their reagents. It is obvious, therefore, that their results, instead of serving as a proper basis for the criticism of a method, are themselves open to serious criticism.

The ammonium chloride wash solution experimented with by Breyer and Schweitzer was the same as that employed by the Association, the preparation of which is described in a succeeding footnote. That a great amount of double decomposition may result with this solution, under exaggerated conditions, has been shown by the work of the Association (U.S. Dept. of Agric., Div. of Chemistry, *Bull.* 43, 1894, pp. 23, 24; and *Bull.* 47, 1895, p. 22) during 1894 and 1895. This fact alone furnishes

Table I.—Comparison of Results on Pure Potassium Chloride by the Lindo-Gladding Method and by the Method of Washing with Alcohol only (1894). (0·1 of a grm. of KCl taken in each Determination. Weights in Grms.).

Analyst.	K_2PtCl_6 washed with alcohol only. KCl found.	K_2PtCl_6 washed with alcohol and ammonium chloride solution. (Lindo-Gladding). KCl found.	Results by washing with ammonium chloride are more (+) or less (−) than those without.
W. A. Powers, Illinois Station	0·10053 0·10114 0·10084	0·10134 0·10159 0·10147	
Average			+0·00063
F. P. Veitch, Maryland College	0·09867	0·09864	−0·00003
J. B. Lindsey, Massachusetts Station	0·10112 0·10066 0·10066	0·10082 0·10097 0·10060 0·10005	
Average	0·10082	0·10061	−0·00021
W. L. Rossman, Michigan Station	0·09957 0·09951 0·09957 0·09933	0·09974 0·09956 0·09971 0·09965	
Average	0·09950	0·09967	+0·00017
J. B. Street, New Jersey station	0·09838 0·09868 0·09871	0·09807 0·09838	
Average	0·09859	0·09823	−0·00036
B. L. Hartwell, Rhode Island Station	0·09960 0·09954	0·09898 0·09913 0·09934	
Average	0·09957	0·09915	−0·00042
K. P. McElroy, United States Department of Agriculture	0·10000 0·10012 0·10006	0·10015 0·10040 0·10028	+0·00022
R. de Roode, West Virginia Station	0·09996	0·09993	−0·00003

TABLE II.—Comparison of Results on Pure Potassium Chloride by the Lindo-Gladding Method and by the Method of Washing with Alcohol only (1895). Weights in Grms.

Analyst.	K_2PtCl_6 washed with alcohol only.			K_2PtCl_6 washed with alcohol and ammonium chloride solution (Lindo-Gladding).		
	Taken. KCl.	Found. KCl.	Error. KCl.	Taken. KCl.	Found. KCl.	Error. KCl.
W. A Powers, Illinois Station				0·3976	0·3954	−0·0022
				0·3872	0·3871	−0·0001
B. L. Hartwell, Rhode Island Station*.	0·4776	0·4780	+0·0004	0·4534	0·4532	−0·0002
	0·4458	0·4463	+0·0005	0·4799	0·4797	−0·0002
	0·4665	0·4668	+0·0003			
	0·5437	0·5442	+0·0005			
G. Wm. Gray, West Virginia Station	0·5114	0·5110	−0·0004	0·5028	0·5002	−0·0026
				0·5080	0·5049	−0·0031
F. P. Veitch, Maryland College	0·5004	0·5002	−0·0002	0·5043	0·5058	+0·0015
	0·5666	0·5685	+0·0019	0·5149	0·5163	+0·0014
	0·5005	0·5027	+0·0022			
W. H. Allen, North Carolina Station				0·2987	0·2989	+0·0002
				0·2987	0·2988	+0·0001
				0·2987	0·2985	−0·0002
J. B. Lindsey, Massachusetts Station.	0·4978	0·4987	+0·0009	0·4978	0·4985	+0·0007
	0·4978	0·4986	+0·0008	0·4978	0·4979	+0·0001
W. G. Brown, United States Department of Agriculture	0·6479	0·6506	+0·0027	0·5550	0·5559	+0·0009
	0·5731	0·5749	+0·0018	0·5557	0·5560	+0·0003
	0·4796	0·4798	+0·0002			
J. P. Street, New Jersey Station.	0·4978	0·4981	+0·0003	0·4978	0·4996	+0·0018
	0·4978	0·4977	−0·0001	0·4978	0·4993	+0·0015
				0·4978	0·4985	+0·0007
E. P. Stone, New Hampshire Station.	0·5022	0·5043	+0·0021	0·5022	0·5043	+0·0021
	0·5883	0·5902	+0·0019	0·5883	0·5902	+0·0019
A. L. Winton, Connecticut Station.	0·4500	0·4508	+0·0008	0·5011	0·5010	−0·0001
	0·5004	0·5013	+0·0009			
	0·5331	0·5338	+0·0007			
	0·5310	0·5313	+0·0003			

* These results have been corrected for an error in the original table.

no suitable basis for the condemnation of the method, provided the amount of error arising in the ordinary course of analysis is practically insignificant.

During the years 1894 and 1895 (U.S. Dept of Agric., Div. of Chem., *Bull.* 43, pp. 17—25; *Bull.* 47, pp. 14—23), one of us (H. J. W.) conducted comparative determinations to learn whether washing with ammonium chloride solution, according to the Lindo-Gladding method, introduced an appreciable error. The analytical work was carried out with the co-operation of the analysts of the Association of Official Agricultural Chemists of the United States, nine taking part during the first year and ten during the second year, no two of them working in the same laboratory or with the same reagents.

In 1894, portions of 4 grms. each of pure potassium chloride were made up to 1000 c.c. with water, and 25 c.c. of this solution, representing 0·1 of a grm. of the salt, were taken for each determination. As the salt contained a small amount of water, which in the portions sent to the different analysts varied from 0·06 to 0·16 per cent, the results have in each case been calculated to correspond with 0·1 of a grm. of the dry material (see Table I.).

The determinations carried out in 1895 were made on solutions of 50 c.c. each, containing from 0·3 to 1·0 grm. of pure potassium chloride, thus exposing to the action of the ammonium chloride solution three to ten times as much potassium platinichloride as in the preceding year.

The salt used was from a new lot containing uniformly 0·45 per cent of moisture; the weights of KCl taken, as given in Table II., represent, however, the dry salt.

In the determinations of both years, each solution of the pure salt was evaporated to a paste with an excess of platinum solution. The residue, after cooling, was stirred for twenty minutes with 30 c.c. of 80 per cent alcohol (sp. gr. 0·8645) and the liquid decanted on a weighed Gooch crucible. The washing was further continued by decantation, using 10 c.c. portions of alcohol and stirring from two to three minutes after each addition.

In some cases the salt, without further washing, was dried at 100° C. and weighed, in others it was first washed with six portions of ammonium chloride solution* of 10 c.c. each, and finally with 80 per cent alcohol, according to the Lindo-Gladding method.

Blank determinations were made by both methods on the reagents.

From the analytical data secured in these determinations, which were given in full in *loc. cit.*, Tables I. and II. have been prepared.

In calculating the results, the total weight of potassium platinichloride obtained in each determination was first corrected by deducting the average weight obtained by the same analyst from the reagents.

* A solution of 100 grms. of ammonium chloride in 50 c.c. of water, which had been shaken for from six to eight hours with 5 to 10 grms. of pulverised potassium platinichloride, allowed to settle over night, and filtered.

For the conversion of K_2PtCl_6 to KCl the factor 0·3069 (Pt 195·0, K 39·11, Cl 35·45) was employed, for reasons stated later.

A careful study of the results given in the tables will make it evident that the potassium platinichloride was very slightly, if at all, acted upon by the ammonium chloride solution. Finkener (*Pogg. Ann.*, cxxix,, p. 697) found that a saturated solution of ammonium chloride at 22° C., when in contact with finely-divided potassium platinichloride for one hour, decomposed but 0·27 per cent of the latter. Since the Lindo-Gladding method, at least as applied to the potash salts, secures the double salt in a granular condition, which, according to Finkener, is not so rapidly acted upon, and since, operating with a Gooch crucible, the ammonium chloride solution is not in contact with the double salt longer than two or three minutes, errors from this source would not be expected to be, and, as numerous results show, are not appreciable. There are few, if any, analytical methods where the precipitate is absolutely insoluble in the wash liquid, and it is absurd to discriminate against the Lindo-Gladding method for theoretical reasons which have no practical significance.

(To be continued).

ON THE SEPARATION OF ALUMINIUM.

By RUDOLF L. LEFFLER, F.C.S.

The "Neutralisation" of Aluminium Chloride.

"NEUTRALISATION" is placed in commas because it must not be taken to mean only the converting of free acid into salts. Although in certain connections a special meaning is well enough understood, one cannot help feeling that the word is not a happy one. It must here be taken to mean not only the "neutralisation" of the acid, but also the continued precipitation of aluminium or ferric hydrate until its undecomposed chloride can no longer dissolve it. In reference to ferric solutions, to "neutralise" frequently carries this special meaning, because it is the state into which such solutions are converted prior to the familiar separations with alkaline salts. The degree to which ferric hydrate may be precipitated and re-dissolved is influenced by the amount of alkaline salts in solution. They tend to hasten the point at which a permanent precipitate forms; but with moderate amounts —and by this I mean such as may be due to the usual amounts of free acid—the proportion between the ferric chloride and the ferric hydrate it holds in solution is generally agreed to be about $Fe_2Cl_6 : 7Fe_2(HO)_6$. With solutions of ferric nitrate the proportion may go up to $Fe_2(NO_3)_6 : 8Fe_2(HO)_6$. It appears also to be indifferent to a solution of ferric chloride, whether it be neutralised in the cold or near boiling-point; the successive precipitates dissolve more rapidly in the latter case, but the proportion $xFe_2Cl_6 : yFe_2(HO)_6$ is the same either way.

The foregoing facts are already well known and utilised daily, but the analogous behaviour of solutions of aluminium does not seem to be as well known.

I find, on turning to the Dictionaries of Watts and Comey, that the above-mentioned behaviour of ferric hydroxide is prominently announced, and respecting the hydroxide of aluminium I find it stated to be insoluble in $FeCl_3$,* soluble in $Fe(NO_3)_3$, $Cr(NO_3)_3$, $Bi(NO_3)_3$, $NaC_2H_3O_2$, &c.; but nowhere do I find it suggested even that it is soluble in its own chloride or other salts. All this notwithstanding it is common to find an instruction to the effect that solutions of aluminium should be neutralised; but in view of the ambiguous meaning of the word it is not easy to say exactly what is meant. Allotting to it, however, the more special meaning we associate with ferric solutions, it remains to be pointed out that the operation is usually performed in the cold, either expressly so (Blair, "Chem. Anal. Iron," p. 232) or in anticipation of the next step, viz., the addition of acetate, which according to a mistaken notion "should be added to the metallic solution when cold, and the whole then heated together" (Crookes, "Select Methods," p. 227). Such conditions make the complete "neutralisation" of aluminium solutions impossible.

With ferric chloride the colour-change tells when the free acid is neutralised, and the deepening colour indicates the progress of the "neutralisation"; but with aluminium chloride such observations cannot be made; one has to depend entirely on the appearance of a permanent precipitate. Quarter of a grm. of aluminium in solution as Al_2Cl_6 would require 27·4 c.c. normal alkali to precipitate it. If we take such a solution (0·25 grm. Al) in the cold, and add, say, soda carbonate from a burette, we shall find the precipitate dissolve readily enough at first, but, after the addition of a few c.c., precipitates are formed which according to one's knowledge of ferric solutions might be called permanent. To quote the regular formulæ, "they do not disappear on vigorous stirring." When about 21·9 c.c. has been added ($= Al_2Cl_6 : 4Al_2(HO)_6$), they go neither with vigorous stirring nor prolonged standing. In fact, they may stand undissolved for a day, but on warming this long-stood turbid solution it dissolves up crystal clear. If we repeat the whole operation with a warm or hot solution of Al_2Cl_6, no permanent turbidity forms until 25·2 c.c. has been added. This proportion is approximately $Al_2Cl_6, 11·5Al_2(HO)_6$. On diluting and boiling the aluminium is not precipitated, so that the Herschel or Schwarzenberg separation would appear to be inapplicable to aluminium. Instead of deepening, a decided turbidity would seem to clear somewhat after this operation. If more carbonate be added, the turbidity—or perhaps better the opalescence—deepens, but no precipitate can be detected; in this way the proportion may reach $Al_2Cl_6 23Al_2(HO)_6$, wanting only an additional 1·20 c.c. to bring down the whole 0·25 grm. metal. Nitrates have less influence in lowering the "neutralisation" point than chlorides. This difference is less marked with ammonia salts than with soda salts.

The "neutralisation" of metallic solutions is a valuable device in effecting the separation of closely-allied elements, because it enables one to use very small amounts of a precipitant which used in excess tends to precipitate those metals one wishes to leave in solution. To explain imperfect acetate separations by saying that the iron, for example, carries down portions of the other metals is wrong, because it associates the error with the precipitation and makes it seem a necessary accompaniment, whereas the iron *must be* precipitated, but no portion of the manganese, say, needs be. The degree to which a solution has been neutralised, and the excess of acetate used, has been shown in a previous communication from this laboratory to be responsible for the better or worse separation of iron from metals of its own group and from copper. There are two current ideas respecting acetate separation of aluminium, founded no doubt on experience. These are:—

I. That aluminium has more tendency than iron to carry down associated metals.

II. That the aluminium itself is not completely precipitated, and therefore it is necessary to examine filtrates, &c.*

In the following section we seek to explain these difficulties and to minimise them:—

The Precipitation of Al_2Cl_6.

Iron may be precipitated in fair accordance with the equation—

$$6NaC_2H_3O_2.3H_2O + Fe_2Cl_6 = 6NaCl + Fe_2(C_2H_3O_2)_6 + 3H_2O.$$

* Doubtful.

* See Fresenius, "Quantitative Analysis," pp. 439–450; "Select Methods," p. 199; Arnold's "Steel-works Anal.," p. 245; Dittmar, "Quant. Anal.," p. 74.

Does an analogous equation represent the precipitation of Al_2Cl_6? Experiment shows that it does not, for if 0·25 grm. of aluminium as chloride be taken instead of precipitating with approximately 4 grms. crystallised soda acetate it will behave in hot solutions as follows:—Add 1 grm. acetate at a time. The second grm. makes the solution opalescent, and this opalescence increases until 6 grms. have been added. Seen casually the solution appears to hold a precipitate, but examined closely no form or body of a precipitate can be seen. The next grm. precipitates the aluminium, and enables us to obtain a clear sparkling filtrate, but on adding ammonia it is seen that *all* the aluminium was not precipitated.

Supposing only 4 grms. of the acetate to have really combined with the aluminium, the presence of alumina in the filtrate may be due to the decomposition of the $Al_2(C_2H_3O_2)_6$ with formation of acetic acid capable of dissolving $Al_2(HO)_6$, and to the excess of soda acetate in which $Al_2(HO)_6$ is said to be soluble. Further, according to the explanation of Brearley (CHEM. NEWS, lxxvi., 223), the necessary excess of acetate would also account for the more incomplete separation of associated metals expressed "by the greater tendency of aluminium to carry down other metals."

Precipitation from Total Hydrates.

"Neutralised" to faint opalescence in *hot* solutions (Na_2CO_3 or NH_4HO), being careful to add at a time only so much as readily dissolves, or, in keeping with familiar experience, the digested $Al_2(HO)_6$ does not dissolve easily, and decomposed the remaining Al_2Cl_6 with the smallest practicable quantity of acetate. It might be anticipated that, having now to decompose only about one-tenth of the former Al_2Cl_6, it could be done with one-tenth of the former acetate, but a considerable excess is needed here also—hence our inability to completely eliminate the errors in every case. It was found that 0·25 and 0·5 grm. Al, completely "neutralised," required 2·25 and 3·75 grms. respectively of soda acetate, or its equivalent of ammonium acetate, to completely precipitate the aluminium; the filtrates were free from alumina when hot, but if allowed to cool during filtering then alumina was always present.

The necessity for the use of these unexpected large amounts of acetate in the precipitation of the "neutralised" solution tells very much against this means of separating aluminium from other elements. Separations from nickel were tried, and minimum amounts of acetate used. It is necessary to keep solutions very hot during filtration, so as to avoid the re-solution of the precipitated $Al_2(HO)_6$. The results were always 1 or 2 per cent too low; moreover, the small amounts of alumina which, with all care, sometimes pass into the filtrate, tend to give low results when the nickel is estimated cyanometrically—a difficulty which at present I have not learned how to completely avoid. From copper the separations are even worse.

The only separation worthy to be called quantitative, and deserving to be noticed, is that from manganese, which it may be recorded is similarly indifferent to moderate excesses of acetate in its separation from iron.

Separations with Sodium Phosphate.

Ni from Al.—Twenty c.c. of a saturated solution of this reagent is required to completely separate half a grm. of aluminium from its "neutralised" chloride. Varying quantities of precipitant, with and without acetic acid, were tried. In each case 0·5 grm. Al and 0·10 grm. Ni was taken; volume of solution, 1 litre; fractional filtration; and the Ni estimated by titrating with KCN (CHEM. NEWS, lxxvi., 49). The precipitates settled quickly, more especially with the larger quantities of acetic acid, and with a little care the filtrate came through the paper (dry ribbed) as quick as one could pour on; they were free from alumina. The figures given are percentage recovery.

Satd. sol. sodium phosphate. C.c.	Acetic acid. C.c.			
	0.	10.	20.	50.
20	89·40	—	—	—
30	45·36	100·0	—	—
50	—	81·0	97·05	99·72
70	—	62·36	91·94	96·41

It appears from these results that the separation can be made only within narrow limits, and that these depend solely upon the proportion beween the phosphate and the acetic acid. The separation of copper and zinc have been experimented with on these lines, but the results were not good.

It must be owned that the behaviour of these completely "neutralised" solutions have not come up to our expectations of them; still we hope to have shown on what grounds "the greater tendency of aluminium than iron to carry down associated metals" rests, and how the most satisfactory acetate separations may be made.

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ON IODIDE OF GLUCINUM.

By P. LEBEAU.

THE formation of iodide of glucinum by the action of iodine on the metal was first pointed out by Wöhler (*Pogg. Ann.*, vol. xiii., 1828), and later by Debray (*Ann. de Chim. et de Phys.*, Series 3, vol. xliv., p. 24, 1855). They describe this compound as a white sublimate, very volatile according to one of them, but less volatile than the chloride according to the other. No work respecting the study of this body has been published since. Further, the preparation of the metal seems to have been sufficient obstacle to prevent further research.

We have been able during our research on the properties of carbide of glucinum, to find a method enabling us to obtain with the greatest ease a considerable quantity of definite crystallised iodide of glucinum. In fact, the vapour of iodine carried by a current of hydrogen, or, better still, dry hydriodic acid, attacks the carbide of glucinum at about 700°, producing a very pure iodide of glucinum. To prepare this iodide with the least trouble, we arrange a tube of Bohemian glass, of 20 or 22 m.m. diameter, on a small gas furnace. The tube should be at least twice as long as the furnace. Five or six grms. of powdered carbide of glucinum are placed in a porcelain boat, or even in the tube itself. A current of hydriodic gas is passed, and the tube then heated to a cherry-red heat. The attack of the carbide goes on in a regular manner, the iodide distils off and condenses in the cold part of the tube in a felty mass of crystals.

When the carbide is very pure, we obtain a perfectly white iodide, which must be collected in a vessel filled with dry carbonic acid gas. If it is of a yellow colour, which is caused by a small quantity of iodide of iron, it suffices to sublime it in a current of dry carbonic acid; the iodide of iron is carried off from the commencement, after which the iodide of glucinum is sublimed in very beautiful crystals.

Analysis has shown us that this body answers to the formula GlI_2 or Gl_2I_6, according to whether we take the atomic weight as 9·08 or 13·8.

				Calculated for GlI_2.
Iodine, per cent ..	96·46	96·37	96·49	96·54
Glucinum	3·49	3·52	3·47	3·45
	99·95	99·89	99·96	99·99

Iodide of glucinum exists in the form of colourless crystals, very easily altered in moist air. Its density at 15° is very close to 4·20. It melts at about 510°, but sublimes

considerably before melting. Its boiling point is somewhere between 585° and 595°; it should apparently therefore be easy to determine its vapour density. We shall return to this subject later on. Iodide of glucinum is insoluble in benzine, toluene, and essence of turpentine, and slightly soluble in sulphide of carbon.

Water reacts violently on iodide of glucinum, giving a soluble hydrated iodide. This property renders the handling of this body a matter of some delicacy, as the least trace of water partially decomposes it. When melted it is much less easily altered, and it is in this form that we have studied its principal properties.

It can be distilled in a current of dry hydrogen without any alteration. Chlorine and bromine decompose it, forming the corresponding compounds, with the liberation of iodine. Fluorine attacks it, forming fluorides of iodine and glucinum.

Fluorine and chlorine act in the cold with incandescence.

Cyanogen reacts on iodide of glucinum below a red heat, and forms a less volatile white substance, producing with water a clear solution having the characteristics of a cyanide. Until now it had not been possible to obtain any cyanic combination of glucinum.

Heated in oxygen, iodide of glucinum takes fire below a red heat. Its vapour burns on contact with air. Sulphur transforms it into a fixed sulphide at a bright red heat; it is decomposable by water.

This experiment clearly shows that there is a sulphurised compound of glucinum. It may be remembered that Debray and Frémy stated that they had not been able to prepare sulphide of glucinum by the ordinary methods.

In a current of nitrogen the iodide distils without changing its composition or appearance. The vapour of phosphorus, on the contrary, destroys it, and forms a combination of phosphorus and glucinum.

Sodium reduces the iodide of glucinum at about 350°; potassium and lithium also react with incandescence at about the same temperature. Alkaline iodides of glucinum are formed. At about 450° magnesium gives an iodide of magnesium and glucinum; this reaction is an important one. Aluminium, silver, copper, and mercury are all without action below a temperature which softens the glass.

Sulphuretted hydrogen does not react at the ordinary temperature, but if it is gently heated hydriodic acid is formed, and a fixed white substance remains, analogous to the sulphide obtained by the action of sulphur. Ammonia gas is absorbed very rapidly in the cold, forming a white powder, much less alterable than the iodide, and giving by analysis the formula $2GlI_2,3NH_3$. On gently heating, a further absorption of ammonia takes place, and the substance melts into a colourless liquid, crystallising on cooling. A prolonged contact gives further rise to another body even richer in ammonia.

Iodide of glucinum reacts on a large number of organic compounds.

It dissolves in the alcohols perfectly free from water, without appreciable heating. With absolute alcohol a crystalline compound is obtained. With ether it also forms a compound, slightly soluble in an excess of ether.

Like the iodide of aluminium, it has no action in the cold on tetrachloride of carbon. It is equally without action on the chloride C_2Cl_4. Acetic anhydride, chloral anhydride, and a very large number of oxygenated organic compounds, give energetic reactions.

Finally, the ammoniacal compounds and the organic bases, notably aniline and pyridine, produce crystallised compounds with iodide of glucinum.

Conclusions.—To sum up; by the action of hydriodic acid on carbide of glucinum we have obtained an iodide of the formula GlI_2, in beautiful transparent crystals. This new iodide is very active, it reacts on a large number of bodies, and serves for the easy preparation of new compounds of glucinum, such as the phosphide, the sulphide, and the cyanide. It also unites with facility with organic compounds.—*Comptes Rendus*, vol. cxxvi., No. 18.

NEW METHODS OF DETECTING AMMONIA IN A GASEOUS ATMOSPHERE.

By G. DENIGÈS.

The detection of ammonia gas in a gaseous atmosphere has been made extremely easy by the use of Nessler's solution, introduced into this atmosphere on a glass rod.

However, the simultaneous presence of amines of the fatty series deprives the mercuro-potassic iodide, in alkaline solution, of its special power; monomethylamine and monethylamine give, in fact, coloured precipitates with this reagent, and the secondary methylic and ethylic amines—to mention only those best known—also form insoluble mercuric compounds.

For these reasons it has appeared to us useful to make known a more specific reaction for ammonia, of which we have made use for some time, as well as reactions which are less characteristic, though interesting, on account of their great sensitiveness. The principle of neither of them is new, but the method of application allows us to qualify these two processes for the detection of ammonia gas, as new.

The first of these consists in plunging the extremity of a glass stirring rod, wetted with hypobromide of soda, into the gas to be tested; on contact with ammonia gas, the wet part of the glass rod gives off a large number of small bubbles of nitrogen gas, so small that they appear as a white sheath round the extremity of the stirrer. At the same time the hypobromite loses its colour.

The property of behaving in this manner to hypobromite of soda belongs *only* to ammonia; in fact, with this reagent the primary amines give a yellowish precipitate, while the other fatty amines cause no notable phenomenon at all.

The two other reactions which we wish to describe belong, like that of mercurous nitrate, as much to the fatty amines as to ammonia gas.

The one is the invert reaction of formol: it is obtained by submitting a drop of commercial formol to the contact of ammoniacal vapours, and then plunging it into 1 c.c. of bromine water acidulated with a drop of acetic acid. In this manner we immediately obtain a cloudiness or a yellow precipitate, produced by a bromine derivative of hexamethylene tetramine.

The other is based on the intense carmine colouration which one drop of an aqueous solution of hæmatoxyline, or of extract of logwood, takes in contact with even very small quantities of ammonia gas.

From the point of view of their degree of specific action we may class the principal reagents of ammonia and the fatty amines in the following manner:—

1. *Hypobromite of Sodium.*

This body gives off bubbles of nitrogen gas under the influence of ammonia. It gives insoluble yellow compounds with the primary fatty amines. It does not react sensibly on the secondary and tertiary amines.

2. *Nessler's Solution.*

Gives a Kermes-red precipitate with ammonia, a yellow precipitate with monomethylamine, and a white precipitate with monethylamine. This latter precipitate rapidly becomes yellow if the reagent is in excess, and regains its white colour with an excess of amine. With dimethylamine and diethylamine it gives a white precipitate; with the latter body the precipitate is soluble in an excess of amine.

Finally, with trimethylamine, and above all in an excess of amine, it gives a white precipitate, rapidly becoming brown.

3. *Mercurous Nitrate, Hæmatoxyline, Formol.*

The first of these bodies in solution becomes black on contact with ammoniacal vapours or fatty amines.

The second takes a carmine colour, and the third gives hexamethylene tetramine, which forms a yellow precipitate with bromine water acidulated with acetic acid.—*Bull. de la Soc. de Pharmacie*, March, 1898.

ON THE ABSORPTION OF NITRIC OXIDE BY FERROUS SALTS.

By M. THOMAS.

It has long been known that all ferrous salts in solution absorb dioxide of nitrogen. The classic work of Péligot (*Ann. Chim. Phys.*, Series 2, xiv., 17, 1803), and the more recent research of M. Gay ("Thèse de Doctorat," 1885), go to prove that we obtain quite definite compounds in the form of solution, with a dissociation-tension at the ordinary temperature. By the evaporation of nitrous solutions, even in an atmosphere of binoxide of nitrogen, we certainly obtain black crystals, but these crystals only contain traces of nitric oxide.

As for the quantity of gas absorbed, the researches of M. Gay led him to the conclusion that the quantity of binoxide of nitrogen absorbed by the salts of peroxide of iron is :—

1. Independent of the nature of the salt.
2. Independent of the degree of dilution of the solution.
3. Proportional to the minimum weight of iron that it contains.
4. A function of the temperature.

This absorption is, 1 molecule of nitric oxide for 2 atoms of iron, at a temperature above 12·5°, and 2 molecules of the gas for 3 atoms of iron below that temperature.

I shall show successively that—

1. All ferrous salts, without exception, possess the same property of absorbing nitric oxide in aqueous solution. (Verification of M. Gay's law).

M. Gay studied the absorption by the chloride, the sulphate, and the ammoniacal sulphate. The absorption takes place in an analogous manner with the most varied salts, such as the chlorate, perchlorate, bromide, bromate, iodide, sulphite, hyposulphite, hyposulphate, &c.

2. All ferrous salts retain this property when another solvent is substituted for water.

The absorption of binoxide of nitrogen by ferrous salts dissolved in different solvents is an important point to know, if we wish to form any hypothesis on the different behaviour of solid or dissolved ferrous salts with nitric oxide. In fact, if we take the aqueous solution of a salt and evaporate it, either *in vacuo* or by any other means, the ferrous salt is left, generally well crystallised, in the form of a hydrate. We are thus brought to the opinion that, in aqueous solutions, the ferrous salt must be present in the anhydrous state, but in combination with water. From this it follows that the absorption of nitric oxide might be caused by the existence of this hydrate in the dissolved state.

I was therefore persuaded to try whether the absorption would take place by substituting other solvents for water.

Solvent used : Alcohol.—Graham (*Phil. Mag.*, iv., 231 and 266) used an alcoholic solution, and showed that nitric oxide was still absorbed by ferrous chloride. *He even showed that the absorption was greater than in an aqueous solution*, and that 1 atom of iron was capable of absorbing 1 molecule of binoxide of nitrogen. Further, all the gas was given off, either by evaporation *in vacuo* or by spontaneous concentration by leaving the solution at the ordinary temperature. It follows, therefore, that the alcoholic nitrous solution has properties entirely comparable with those of the aqueous solution.

Not only the chloride, but all the salts tried by me behaved in the same manner; for instance, the bromide and the iodide. However, as Graham has shown that the ferrous chloride was able to absorb vapour of alcohol as well as aqueous vapour, and as I, on the other hand, have shown that the chloride and bromide react chemically on alcohol, giving, without doubt, some double compounds analogous to the hydrates, it might here again be objected that the absorption might be caused by these compounds in solution, and not by the ferrous salt itself.

Solvent used : Ether.—If we reduce a solution of ferric chloride or bromide by binoxide of nitrogen, *the ferrous salt formed remains in solution*, and the solution is strongly blackened by the quantity of nitric oxide it retains. By evaporation the solution becomes syrupy, and voluminous crystals are seen, which the microscope shows to be in the form of prisms of a bright red colour forming macles; this represents the product of the reaction of the ferrous chloride on the ether. By using acetic acid and bromide of ethylene, which leaves by evaporation the anhydrous ferrous salt, we can, on the contrary, show that the absorption of gas is really due to the ferrous salt itself.

Solvents used : Acetic Acid, Bromide of Ethylene.—The acetic acid used was crystallised at 16·25°, and was then sufficiently pure for the experiments.

The absorption of nitric oxide takes place in acetic solution, the same as in aqueous, alcoholic, or ethereal solution.

Bromide of ethylene behaves in every respect just like acetic acid.

3. The absorption of nitric oxide is variable according to the solvent used.

This result is found from the figures given for the absorption by ferrous chloride in aqueous solution by M. Gay, and in alcoholic solution by Graham.

Absorption in Aqueous Solution (Gay).

	For 56 of iron.	Per cent.
From 4° to 12° ..	19·48	34·78
„ 16° to 22° ..	15·00	26·78
To 25°	10·80	18·92

Absorption in Alcoholic Solution (Graham).

The information given in Graham's papers shows the proportion of binoxide of nitrogen to be greater than 50 per cent.

Furthermore, I have repeated these experiments, and determined the quantity of gas absorbed exactly. The absorptions were determined volumetrically; the following was the method employed :—Into a graduated tube resting in the mercury trough, a certain volume of ferrous chloride of known strength was introduced. By the aid of a second graduated tube a known volume of binoxide of nitrogen was added. The gas was prepared by the action of nitric acid on mercury; the use of copper and nitric acid gives not only protoxide of nitrogen as an impurity, but also nitrogen which cannot be got rid of. I will now give a few figures :—

I. 12·2 c.c. of a solution containing 4·6 grms. of iron per 1000 c.c. absorbed 21·5 c.c. of nitric oxide at a temperature of 17°.

II. 12·5 c.c. of the same solution absorbed 23·4 c.c. at a temperature of 15°.

This gives for NO in percentage of iron :—

I. At 17° .. .. 51·37 per cent.
II. At 15° .. .. 54·57 „

These figures, it will be seen, are quite comparable with those obtained by Graham.

Remarks.—The gaseous volumes measured were brought to 0°. To determine the exact volumes not absorbed the readings were made at a pressure of 760 m.m., augmented by the pressure of the maximum tension of the solvent.

This tension, negligible in the case of water, is not so in the case of alcohol.

In a succeeding paper I shall discuss the absorption of nitric oxide by ferrous bromide and ferrous iodide.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 10.

ON THE CONDITION OF OXIDATION OF MANGANESE. PRECIPITATED BY THE CHLORATE PROCESS.*

By F. A. GOOCH and MARTHA AUSTIN.

Hannay (*Journ. Chem. Soc.*, xxxiii., 269), who was the first to propose the precipitation of manganese from its solution in nitric acid by the use of potassium chlorate, states that precipitation is complete, but that the oxide produced is not of constant composition. While, therefore, precipitation by this method serves an excellent purpose in separating manganese from other substances, it was Hannay's opinion that reliance cannot be placed upon the determination of the oxygen value of the oxide to estimate the manganese. Beilstein and Jawein (*Ber. d. Chem. Gesell.*, xii., 1528), who proposed the same method, subsequently, regarded the precipitate as the oxide MnO_2. Hannay's reaction was developed, independently, by Hampe (*Chem. Centralblatt.*, 1885, 714) and Ford (*Trans. Inst. Am. Min. Engineers*, ix., 347) into the method which is now known as the "chlorate process" for the estimation of manganese. The discussion of the exact condition of the precipitated oxide was very active ten years ago, and occasional echoes of it are heard at the present day; and yet, in all this discussion we find no account of an adequate test of the process upon an exact amount of a salt of manganese known to be pure. The discussion for the most part has centred about the degree of oxidation of the precipitate, but there is obviously another condition to be taken into account, viz., the possibility of the mechanical inclusion of the comparatively insoluble chlorate in the precipitated oxide. As to the existence of the latter source of error we have had in the course of our work very strong affirmative evidence, the apparent condition of oxidation of the precipitate being sometimes so high as to be otherwise inexplicable. This difficulty does not occur, however, when a more soluble chlorate is chosen to do the work of oxidation, and we have found quite as convenient and much safer the substitution of sodium chlorate for the comparatively insoluble potassium chlorate. Besides, the rapidity with which the sodium chlorate is decomposed makes its use an advantage.

With regard to the completeness of the precipitation, our experience has shown that with due precaution the method is practically perfect. Thus, after boiling manganous nitrate (free from chlorides and sulphates) with strong nitric acid (85 c.m.^{3}) and sodium chlorate (5 grms.) for five minutes, adding subsequently 15 c.m.^{3} of the nitric acid and a few crystals more of the sodium chlorate, and discontinuing the heating as soon as the liquid again boils, the insolubility of the manganese is so great that no more than insignificant traces may be recovered from the filtrate after cooling, filtering upon asbestos, and washing with water. The test for manganese in the filtrate and washings was made after evaporation and solution of the residue in distilled water by treating the hot solution with bromine and ammonia. In the first division of the table below are results obtained by treating the manganese precipitated from the filtrate with potassium iodide and sulphuric acid, the iodine set free being determined by sodium thiosulphate. In the second series, the precipitated manganese dioxide was reduced by a known amount of decinormal arsenious acid and the amount remaining unoxidised was estimated by titration with iodine in the presence of acid potassium carbonate.

Table I.

$MnSO_4$ taken. Grm.	Mn found by KI treatment in filtrate. Grm.	Mn found by As_2O_3 treatment in filtrate. Grm.
0·3361	none	—
0·3361	none	—
0·3361	0·00006	—
0·3361	0·00005	—
0·3361	0·00002	—
0·3361	0·00008	—
0·3361	none	—
0·4128	—	0·00003
0·4128	—	0·00003
0·4128	—	trace
0·4128	—	trace

It will be seen that in no case did the manganese which escaped precipitation—that which corresponded to the iodine freed or the arsenious acid oxidised—exceed 0·0001 grm. Plainly, this modified method of handling the chlorate process may be trusted to precipitate the manganese with gratifying rapidity and approximation to completeness. Our experience has shown plainly that prolonged boiling results in a considerable loss of manganese (from 0·0010—0·0030 grm.). This, we think, is due to the solvent effect of the lower oxides of nitrogen naturally produced (as is always the case in boiling nitric acid) after the chlorine dioxide has been thoroughly expelled. An excess of the chlorate at the end of the boiling seems to be essential and a slight yellow colour in the solution, due to chlorine dioxide, is a favourable indication rather than the reverse. We find it best to filter the undiluted nitric acid, under pressure, upon asbestos on a perforated cone with a filtering surface of about 40 sq. c.m. The dilution of the nitric acid before filtration tends to produce some solubility of the manganese, and the loss then introduced, though trifling if the filtration is rapid, may be considerable if the process of filtration is prolonged, as is the case in the method approved by the Verein der Deutschen Eisenhütteleute (Von Reis, *Zeit. Angewandte Chem.*, 1891, 376).

Our experiments upon the chlorate process have been made with manganous chloride prepared as detailed in a former paper, viz., by boiling manganous chloride with manganous carbonate, precipitating the filtered solution with ammonium sulphide, dissolving the washed manganous sulphide in dilute hydrochloric acid, precipitating the solution thus obtained with sodium carbonate (after boiling out hydrogen sulphide), dissolving the greater part of the manganous carbonate (thoroughly washed by repeatedly boiling it in successive portions of water) in the least amount of hydrochloric acid, and boiling the solution thus obtained with the remainder of the pure carbonate and filtering. The standard of the solution thus prepared, neutral and probably very pure, was fixed by evaporating definite portions with sulphuric acid and weighing the residue as the normal sulphate, in accordance with the procedure outlined in a former paper (*Am. Journ. Science*, IV., v., 209; Chem. News, lxxvii., 255).

Any method by means of which the oxidising power of the higher oxygen compounds of manganese is discoverable may, obviously, be employed to determine the condition of the manganese precipitated in this chlorate process. Convenient processes for the determination of the available oxygen in the higher oxides of manganese are the iodometric methods of Bunsen and Pickering. Bunsen's method is applicable to any of the higher oxygen compounds of manganese—though somewhat inconvenient, because it involves the distillation of the chlorine liberated by the action of strong hydrochloric acid upon the substance and its collection in potassium iodide, the iodine thus set free being estimated by standard thiosul-

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science* vol. v., p. 260.

phate. According to Pickering's method (*Journ. Chem. Soc.*, xxxvii., 128), the higher oxide is treated immediately with potassium iodide and hydrochloric acid, and the iodine liberated is estimated by sodium thiosulphate. Plainly, the latter method is limited to the treatment of the less refractory or more finely comminuted oxides, and it fails in the presence of ferric salts and all other substances capable of liberating iodine from the acidified iodide.

Still another general iodometric method for determining the oxygen value of the higher oxides of manganese is suggested by Deshayes's titration of permanganic acid in nitric acid by means of standard arsenious acid (*Bull. Soc. Chim.*, xxix., 541). Our experience in following out this idea shows that the precipitated oxides of manganese, as well as the soluble permanganate, may be easily reduced with the aid of gentle heating by arsenious acid in the presence of sulphuric acid, and that the determination of the excess of arsenious acid by titration with iodine after neutralisation of the free sulphuric acid by an alkaline carbonate gives exact data for estimating the oxidising power of the manganese compound. We found, however, that if the iodine is allowed to come into contact with the manganous carbonate thrown down by the alkaline carbonate, as is inevitable for at least short intervals during the titration of the arsenious acid in presence of the floating carbonate, the danger arises of more or less re-oxidation of the manganous carbonate by the iodine and the consequent introduction of error. Fortunately the difficulty may be obviated by adding to the solution, while still acid, enough tartaric acid or alkaline tartrate, to prevent the precipitation of the manganese in the subsequent neutralisation by the bicarbonate.

(To be continued).

THE SEPTIC TREATMENT OF SEWAGE.

The Local Government Board have decided to give their approval to the scheme submitted to the Exeter City Council by Mr. Cameron, the City Surveyor, for disposing of the sewage of Exeter by the Septic system at an estimated expenditure of £40,000.

In their letter to the Exeter City Council, the Local Government Board state:—"The Board have directed their inquiries, with the view of determining two questions. In the first place, they desired to ascertain whether the final effluent obtained by the Septic process was uniformly of such a character as to permit of its discharge into the river without further treatment on land. If not, was the process a sufficient preliminary to the treatment of the sewage on land; and was the land possessed by the Exeter City Council suitable in quantity and quality? The Local Government Board have come to the conclusion that, if the Septic process be adopted, a further treatment of the sewage on land will still be required previous to the effluent being discharged into the river. The Board, however, are not unwilling to accept, by way of experiment, the adoption of the process recommended by the City Surveyor as a method of treatment preliminary to further treatment on land. The Local Government Board will approve of the scheme on the distinct understanding that the City Council, in adopting this system as an experimental substitute for the ordinary process of chemical precipitation, will accept the entire responsibility for the experiment, and will give an undertaking that, in the event of the process failing to give satisfactory results when applied to the sewage of the entire city, they will adopt in its place some process of treating the sewage with chemicals combined with artificial filtration. The Board understand that the tanks can readily be made available for use as part of such a system. With regard to the quantity of land required, the Board would point out that the Exeter City Council must possess themselves of land for treating the effluent equal to that which is required under schemes in which chemical precipitation and artificial filtration are adopted; that is to say, an acre for each 2000 of the population. The Board will further require the Council to protect themselves from floods, and must therefore stipulate for flood tanks at Duck's Marsh and Belle Isle."

KRYPTON.

On Monday last, June 6th, 1898, the discovery of yet another element was announced, in a communication made by Prof. Ramsay, of London, to the Academy of Sciences of Paris. The communication was read to the Academy by M. Berthelot. This new element is a gas, and makes a fifth constituent of the atmosphere; it is, however, present in very minute quantities, viz., one part in ten thousand of its volume. Krypton belongs not to the argon, but the helium group; its density is greater than that of nitrogen, being, according to the corrected measurement, 22·47.

The discovery of this new gas is in a way due to the kindness of Dr. Hampson, who supplied Prof. Ramsay with about 750 c.c. of liquid air; this was allowed to evaporate away slowly, until not more than 10 c.c. were left. This gaseous residue was freed from oxygen and nitrogen, and then sparked in the presence of oxygen and caustic soda, when a spectrum was obtained showing the argon lines feebly, but in addition to this a new spectrum was observed.

This spectrum is not yet entirely disentangled from the spectrum of argon; it is, however, characterised by two very brilliant lines, one almost identical with D_3, and another one very strong in the green.

Measurements made with a grating of 14,438 lines to the inch give:—

$D_1 = 5895{\cdot}0$
$D_2 = 5889{\cdot}0$
$D_3 = 5875{\cdot}9$
$D_4 = 5867{\cdot}7$

The green line, which is comparable with the helium line in intensity, has the wave-length 5568·8, and the somewhat weaker line which accompanies it has the wave-length 5560·6.

The wave-length of sound was determined in the gas by the method described in the "Argon" paper. The data are—

	I.	II.	III.
Wave-length in air ..	34·17	34·30	34·57
„ in gas ..	29·87	30·13	—

Calculating by the formula—

λ_2 air × density air : λ_2 gas × density gas :: y air : y gas
$(34{\cdot}33)^2 \times 14{\cdot}479 : (30)^2 \times 22{\cdot}47 :: 1{\cdot}408 : 1{\cdot}666$

it is seen that, like argon and helium, the new gas is monatomic, and therefore an element.

The atomic weight of krypton will probably be found to be 80.

The Working of Dropping Electrodes.—Wilhelm Palmaer.—The apparatus is drawn and described. The mercury is contained in a reservoir connected by a long tube with the capillary funnel, from which it drops through an aqueous solution of calomel on to the other electrode. The experiments are a practical investigation of Nernst's theory of dropping electrodes, and the results fully confirm the theory. The migration of the ions is directed by the contact of a metal and a solution, without breaking the circuit by other than chemical means. The above theory gives, as Nernst has pointed out, a method free from objection of estimating the potential difference between the mercury electrode and the electrolyte.—*Zeit. für Physikalische Chemie*, xxv., No. 2.

THE BRITISH ASSOCIATION.

The Sixty-eighth Meeting of the British Association for the Advancement of Science will commence in Bristol on Wednesday, the 7th of September, 1898. The following arrangements have been made for the meeting:—

The General Committee will meet on Wednesday, the 7th of September, at 1 p.m., for the election of Sectional Officers, and the despatch of business usually brought before that body. On this occasion the Council will present a Report, giving an account of their proceedings during the past year. The Committee will meet again on Monday, September 12, at 3.15 p.m., for the purpose of appointing Officers for the meeting at Dover in 1899, and of deciding on the place of meeting in 1900. The concluding meeting of this Committee will be held on Wednesday, the 14th of September, at 1 p.m., when the Report of the Committee of Recommendations will be received.

The first General Meeting will be held on Wednesday, the 7th of September, at 8 p.m., when the President will deliver an Address; the Concluding Meeting on Wednesday, the 14th of September, at 2.30 p.m., when the Association will be adjourned to its next place of meeting.

At two Evening Meetings, which will begin at 8.30 p.m., Discourses will be delivered: on the 9th of September by Professor W. J. Sollas, M.A., F.R.S.; and on the 12th of September by Herbert Jackson, Esq.

There will also be other Evening Meetings, at which opportunity will be afforded for general conversation among the members.

Sections.—The following are the titles of the Sections and the names of the members who have been nominated by the Council for the office of President of Section:—

Section.	
A. Mathematical and Physical Science	Prof. W. E. Ayrton, F.R.S.
B. Chemistry	Prof. F. R. Japp, Ph.D., F.R.S.
C. Geology	W. H. Hudleston, Esq., M.A., F.R.S.
D. Zoology	Prof. W. F. R. Weldon, F.R.S.
E. Geography	Col. George Earl Church.
F. Economic Science and Statistics	Jas. Bonar, Esq., M.A., LL.D.
G. Mechanical Science ..	Sir John Wolfe-Barry, K.C.B., F.R.S.
H. Anthropology	E. W. Brabrook, Esq., C.B., F.S.A.
K. Botany	Prof. F. O. Bower, D.Sc., F.R.S.

An International Conference on Terrestrial Magnetism and Atmospheric Electricity, which will also meet at Bristol, will be associated with Section A as a Special Department under the presidency of Prof. A. W. Rücker, Sec. R.S.

The different Sections will assemble in the rooms appointed for them, for the reading and discussion of Reports and Papers, on Thursday, September 8; Friday, September 9; Saturday, September 10; Monday, September 12; and Tuesday, September 13.

The acceptance of Papers, and the days on which they are to be read, are determined, as far as possible, by the Organising Committees of the several Sections before the beginning of the Meeting. It is therefore necessary, in order to give an opportunity to the Committees of doing justice to the several Communications, that each Author should prepare an Abstract of his Paper, of a length suitable for insertion in the Annual Report of the Association, and the Council request that he will send it, together with the original Paper, by book-post, on or before August 1, addressed thus—"General Secretaries, British Association, Burlington House, London, W. For Section.....', Authors who comply with this request, and whose Papers are accepted, will be furnished before the Meeting with printed copies of their Abstracts. If it should be inconvenient to the Author that his Paper should be read on any particular days, he is requested to send information thereof to the Secretaries in a separate note. Abstracts sent in after August 1, but before the end of the Meeting, will appear in the Report, but cannot be printed beforehand.

Reports on the Progress of Science, and of Researches intrusted to Individuals or Committees, must be forwarded to the Secretaries, for presentation to the Organising Committees, accompanied in each case by a statement whether the Author will be present at the Annual Meeting.

No Report, Paper, or Abstract can be inserted in the Report of the Association unless it is in the hands of the Assistant General Secretary before the conclusion of the Meeting.

Tickets.—The Reception Room will be opened on Monday, September 5, at 2 p. m., and on the following days at 8 a.m., for the issue of Tickets to Members, Associates, and Ladies, according to the statement given below, and for supplying Lists and Prices of Lodgings, and other information to strangers on their arrival. No Tickets will be issued after 6 p.m.

Members and Associates.—New Members and Associates can join the Association on the following conditions:—

I. New Life Members for a composition of £10, which entitles them to receive gratuitously the Annual Reports of the Association which may be published after the date of payment.

II. New Annual Members for a payment of £2 for the first year. These receive gratuitously the Annual Reports of the Association for the year of admission and for every following year in which they continue to pay a Subscription of £1 without intermission.

III. Associates for this Meeting only for a payment of £1. They are entitled to receive the Report of this Meeting at two-thirds of the publication price. Associates are not eligible to serve on Committees or to hold any office.

Ladies may become Members or Associates on the same terms as Gentlemen, or they can obtain Ladies' Tickets (transferable to Ladies only) on payment of £1.

E. A. Schäfer.
W. C. Roberts-Austen, } General Secretaries.
G. Griffith, Assistant General Secretary.

The Preparation of Gentianose.—E. Bourquelot and L. Nardin.—The root of gentian is treated with a hot solution of alcohol at 95°; if the root contains a soluble ferment capable of hydrolysing the gentianose, it must be destroyed. Gentianose exists as perfectly white flakey crystals, which contain no water of crystallisation; it is easily soluble in water, and melts at from 207° to 209°. —*Journ. de Pharm. et de Chim.*, vii., No. 6.

Refraction and Dispersive Power of Silicon in its Compounds.—Gino Abati.—It has already been proved that silicon shows remarkable difference in refractive power, according to the element with which it is combined, but very few compounds have been examined, and the author makes a close investigation of the subject. He used silicon chlorides and bromides, as well as silicon methylate, orthosilicic methylester, propylester, and a solution of silicic hydrate. The refractive indices are taken for lines $H\alpha$, $H\beta$, $H\gamma$, and D of the spectrum, and the specific gravities relative to water at 4°. The results obtained show that the value of the refraction constant is not always dependent on the constitution of the compound, but it depends in a much higher degree on the nature of the elements taking part in the compound.—*Zeit. fur Physikalische Chemie*, xxv., No. 2.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

The Soirée held at the Royal Society's Rooms at Burlington House, on Wednesday evening last, June 8th, was very well attended, the fact of its being a Ladies' night adding much to the enjoyment of the Fellows. The guests were received by Lord Lister and Sir John and Lady Evans.

There were, as usual, a number of interesting exhibits, the apparatus shown by Prof. Roberts-Austen for the Micro-photography of Metals being of great interest.

The Automatic Telephone Exchange System, which proposes to do away with the autocrats of the present Exchanges, was shown by Mr. C. Vautin. We shall be glad when its adoption in London is an accomplished fact.

Two models were shown by Prof. J. Norman Collie, to represent in space the arrangement of the Carbon and Hydrogen Atoms in the Benzene Molecule. In one model the carbon atoms are represented by large, and the hydrogen atoms by small spheres; by rotating the carbon atoms the hydrogen atoms are seen to approach the centre in two sets. In the second model the tetrahedra represent the carbon atoms.

An Interference Dilatometer for the measurement of the thermal expansion of solids, by Fizeau's method of observing the displacement, with rise of temperature, of dark interference bands, was exhibited by Mr. A. Tutton.

Prof. Ramsay showed the spectrum of the new element Krypton; further particulars of this discovery will be found on page 270.

Sir Richard Thorne and Dr. Copeman showed a number of tubes and plates illustrating the Bacteriology of Calf Vaccine Lymph, with special reference to the preparation of Aseptic Glycerinated Lymph; the cultivations and plates prove conclusively that the tubercle bacillus is killed by the glycerin, while the efficiency of the lymph is not affected.

An Improved Heliostat, in which slow motions, enabling the observer to adjust the direction of the reflected beam without taking his eye from the spectroscope (or other instrument), was shown by Dr. Johnstone Stoney. In the adjoining room was the Range-finder, exhibited by Profs. Barr and Stroud: the accuracy of this instrument, under good conditions of working, may be taken as 1 per cent at 3000 yards.

Two demonstrations were given in the Meeting Room —one by Prof. Hele Shaw on the Flow of Water, and the other by Sir Norman Lockyer on the recent Total Solar Eclipse observed at Viziadrug.

SOCIÉTÉ D'ENCOURAGEMENT POUR L'INDUSTRIE NATIONALE.

May 19, 1898.

M. Carnot, President, in the chair.

MM. Auguste and Louis Lumière presented some stereoscopic proofs, printed in colours, obtained by the indirect method. They were obtained by means of three screens, orange, green, and violet, through which three separate photographs were taken. The printing and the superposition of the monochromes were effected by the use of a photographic process with bichromated gums, based on the following fact:—Strong bichromated gum, soluble in the cold, which does not give half-tones when employed alone, acquires this property when insoluble substances are added under certain conditions. If, for example, 5 per cent of bichromate of ammonium and from 5 to 10 per cent of emulsioned bromide of silver is added to a 10 per cent solution of strong gum, and this preparation is spread over a plate of glass, a sensitive surface is produced, which can be exposed under the negative it is desired to reproduce; the plate is then washed with cold water, and a barely visible image is then obtained, formed by the gum which has been made insoluble; this can be coloured as desired. The bromide of silver is removed by hyposulphite. This process gives proofs of all colours, with all the grades of tints present in the negative.

A paper was then presented on behalf of M. Charpy, on "*White, or so-called Anti-friction, Metals.*"

Followed by a communication by M. Saglio, on "*Enamels of High Dilatation.*"

If the boric acid and the lime in the mineral "pandermite" tend to increase the dilatation of an enamel, they also increase its solubility in acids. The difficulty of the problem lies, therefore, in the union of two properties which appear to be contradictory—high dilatation and insolubility. Trials have, however, proved that the production of enamels with a high dilatation, without the use of lead salts, and with a very satisfactory insolubility, is not impossible. The results of a large number of experiments show that—(1) Silica, kaolin, petalite, and zircon give the enamel infusibility and insolubility, but lower the dilatation. (2) Phosphate of lime increases the dilatation, gives viscosity to the fused enamel, and also gives it a certain amount of insolubility. (3) Cryolite, fluorspar, and above all rutile, increases the dilatation and the fusibility of the enamel. Phosphoric acid would seem to be particularly interesting, as it appears to combine high dilatation with insolubility.

NOTICES OF BOOKS.

A Manual of Quantitative Chemical Analysis. By E. F. Ladd. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1898. Pp. vi.—82. 12mo.

The author of this booklet, who is Professor of Chemistry in the North Dakota Agricultural College, and Chemist to the Government Experiment Station, Fargo, North Dakota, explains that it is intended for the use of beginners, and that the methods have been selected to advance the student from the simple analysis to the more complex and difficult, as well as to develop the reasoning power of the student. On this account "explanations of details and reactions have been largely omitted, and the series of questions at the end of each method will test the student's knowledge of chemistry." The course of experimental work covers a good deal of ground:—Gravimetric analysis of metals, acids, and a few simple minerals; volumetric analysis of alkalies and acids; analysis of ashes and soils; analysis of ores of iron, zinc, and lead; electrolysis; examination of sugars, starches, and foods; water analysis; and urine analysis (all within 76 pages).

The author's method of treating the subject will appear from a summary of the first example. Directions are given for dissolving 0·3 grm. pure iron wire in nitric acid, precipitating with ammonium hydrate, filtering, washing, drying, igniting, and weighing as Fe_2O_3. Then follows an equation (which the author calls a "formula") for calculating the percentage of iron obtained. Three questions succeed:—(1) Why dry ppt. before igniting? (2) Why add HNO_3? (3) Is there any danger of loss by volatilisation of the iron? Question No. 2 will doubtless puzzle beginners, and might suggest the answer: "Why *not* add HNO_3?" To dissolve iron in nitric acid without adding the acid is a poser!

The author commends cleanliness and neatness, and recommends "freely using a sponge," which ought to be unnecessary if the student is really neat and avoids spilling liquids on his desk. Better than a sponge would

be to cover the desk with a sheet of white paper, and give strict injunctions not to soil it.

The author uses the rules for spelling recommended by the American Association for the Advancement of Science, except where he relapses through forgetfulness, as on p. 29. He uses the objectionable word *titre*, and the fact that he always places it within quotation marks does not abrogate the objection. In the Table of Elements Ramsay appears as "Ramsey" twice, and Hjelm as "Hjehu," but the book is well printed and has an Index.

H. C. B.

The Arrangement of Atoms in Space. By J. H. VAN 'T HOFF. Second Edition, Revised and Enlarged. Translated and Edited by ARNOLD EILOART. London, New York, and Bombay: Longmans, Green, and Co. 1898. Pp. 211.

IT is twenty-one years since the first edition of this book was published, and the original views with regard to Stereo-chemistry still survive, though the application of them has made great strides during the interval. The possibility of tetrahedral grouping was first suggested to the author by the researches of Pasteur, who had shown the connection between optical activity and crystalline form, and this led to the idea that isomers of opposite rotatory power correspond to an asymmetric grouping and to its mirror-like reflection.

The fundamental idea of Stereo-chemistry is, that in a system of atomic mechanics the molecule will appear as a stable system of material points, and what is dealt with in this volume is nothing else than the spatial—or the real—position of these points, which are the atoms. The asymmetric carbon atom takes first place in the book; and in Chap. II. we have to deal with the division of the inactive mixture, and the temperature of conversion, considered principally with regard to the two tartrates of Pasteur: this is soon followed by a chapter on the position of the radicals in stereomers, the unsaturated carbon compounds and ring formation. With regard to the numerical value of the rotatory power, it must be remembered that this depends on three things—on the wave-length of the light, on the solvent, and on the temperature. The first thing to do is to find the best conditions for obtaining comparable numbers, and here, it is pointed out, it is most essential to take note of the new conception of solution; ring formation appears to have a very extraordinary influence both on the magnitude and the sign of the rotation, the change being first noticed in the case of lactic acid, $[\alpha]_D + 2°$ and $+3°$, while the lactone—

$$CH_3CH-CO \atop \quad\quad O$$

has the enormous rotation $[\alpha]_D = -86°$.

After a short chapter on the Stereo-chemistry of Nitrogen Compounds, the book closes with an Appendix by Alfred Werner, on the Stereo-chemical Isomerism of Inorganic Compounds.

The whole book is written in a clear and distinct manner, and will certainly prove to be a valuable help to the comprehension of Stereo-chemistry, and also the work to which the theory has long ago given rise.

Introduction to the Study of Organic Chemistry. By JOHN WADE, B.Sc. (Lond.), London: Swan, Sonnenschein, and Co., Lim. 1898. Pp. 460, and 11 Illustrations.

THE subject of Organic Chemistry is, in the volume now before us, treated experimentally from the beginning, the hypotheses and theories being introduced later on as they are required. There is great advantage in thus dealing with a matter; does not an old saw tell us that "an ounce of practice is worth a pound of theory"? As with engineering, where the 'prentices have to go through the shops as a preliminary to more serious study, so with chemistry, practice should precede theory, though, until quite recently, we are afraid this has not often been the case in view of the always looming written examination.

The book is divided into three principal parts. Part I. Typical compounds of simple construction, subdivided into four sections and nineteen chapters. Beginning with the preparation of pure alcohol by simple distillation, we pass on to the general reactions of alcohol, and the preparation of the ethyl, methyl, and fatty derivatives, the aldehyds, acetone and secondary propyl alcohol, &c.

Part II. is entitled "Aliphatic or Open Chain Compounds," and consists of five sections and nineteen chapters; the first, *i.e.*, Chapter XX., is on the halogen substitution products; then come the hydroxy-substitution products, the glycerol-mesoxalic series, the four lactic acids, &c. Section VIII. deals with the six-carbon derivatives, or sugars; and Section IX. with the aliphatic derivatives of nitrogen, &c.

Part III., the "Aromatic, or Ring Compounds," contains seven sections and twenty-eight chapters. We have first the benzene and phenyl radical, the benzyl-benzoic group,—in fact, all the benzenoid compounds.

It will be noticed from their large number, viz., sixty-seven, that the chapters have purposely been made short; there is very good reason in this, as, the subject being more subdivided, the student is better able to assimilate the ideas than if he had to go on wading through page after page, hardly knowing when to break off.

At the end of nearly every chapter there is a chart, showing the typical formation of the molecules of the bodies just described, and their relations one to another.

There are two appendices. Appendix I., "Laboratory Notes," is full of all kinds of useful instruction, and hints on manipulation in carrying out the various experiments described in the preceding chapters; and Appendix II., on "Qualitative Analysis," in which an excellent scheme is given which will be found useful in determining the nature of artificial mixtures of certain organic compounds, a list of which is given, with inorganic acids, bases, &c., the tests for the individual compounds being given in Appendix I.

There are two indices, a Name Index of six columns and a Subject-matter Index of twenty-nine columns.

The book should be a valuable addition to those already in use by the University and Technical School Student.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 16, April 18, 1898.

Some Derivatives of Tetramethyl-diamido-benzophenone—E. Grimaux.—To prepare the di-nitrated derivative—

$$CO\begin{matrix}\diagup C_6H_3(NO_2)N(CH_3)_2 \\ \diagdown C_6H_3(NO_2)N(CH_3)_2\end{matrix}$$

of tetramethyl-diamido-benzophone, the ketone is dissolved in 20 parts of ordinary sulphuric acid and two molecules of nitrate of potassium added; after standing for twenty-four hours it is poured into water, and the solution saturated with carbonate of sodium. The precipitate is an orange powder and separates out in small crystals from warm water; they resemble bichromate of ammonia in appearance and melt at 165°—166°. The bromide derivative is prepared by dissolving the ketone in 10 parts of chloroform and adding two molecules of bromine. The chloroform is driven off on the water-bath

and the residue taken up by hydrochloric acid diluted with its own volume of water. The acid solution is precipitated by ammonia, and the white precipitate, after desiccation, is crystallised in 25 parts of boiling alcohol. The di-bromised ketone—

$$CO\begin{matrix}/C_6H_3BrN(CH_3)_2\\ \backslash C_6H_3BrN(CH_3)_2\end{matrix}$$

crystallises in hard, brilliant prisms, fusible at 130°—131°. Both these derivatives have been condensed with dimethylaniline and phenyl-α-naphthylamine by the chloride of phosphorus method and have given new colouring matters.

Influence of Temperature on Chemical Reactions.—Albert Colson.—Though pyrophosphate of silver is not attacked by dry sulphuretted hydrogen at the melting-point of ice, at from 15° to 20° the absorption of SH_2 is noticeable, being equal to 2 m.m. of mercury in twenty-four hours; at 100° it reaches 200 m.m. in one minute with the mean pressure of the gas at about 600 m.m. The ortho-phosphate of zinc, $(PO_4)_2Zn_3$, when well dried, behaves in the same way as the silver salts. To determine how the mass of gas absorbed varied at a constant temperature with a diminishing pressure, a certain quantity of SH_2 was put in contact with a large excess of phosphate of zinc at 100°. In fifteen minutes an absorption was noted of—

6·3	c.c. of SH_2	at a mean pressure of	600	m.m.
4·6	„	„	430	„
3·2	„	„	330	„

From this it is seen that the mass of sulphuretted hydrogen decomposed by phosphate of zinc, in a unit of time and at a constant temperature, is proportional to the square of the pressure. The salts of copper are attacked more vigorously than those of silver, but their decomposition does not disengage more heat.

On the Phosphoric Mono-Ethers.—J. Cavalier.—The author finds that monoethylphosphoric acid gives two series of salts, the neutral $PO_4(C_2H_5)M_2$ and the acid $PO_4(C_2H_5)MH$, and that with regard to methyl orange and phthalein they behave like phosphoric acid.

On the Alkaline Sulphantimonites.—M. Pouget.—By acting on the monosulphides of sodium and ammonium with sulphide of antimony, the normal sulphantimonite, SbS_3Na_3, is obtained; when crystallised it acts powerfully on polarised light. The action of sulphide of ammonium is different to that of sodium and of potassium; the solution is, in fact, only partial, a mass of crystals being formed, while the normal sulphantimonite remains in the mother-liquor.

Zeitschrift für Physikalische Chemie,
Vol. xxv., No. 2.

The Dissociation of Dibasic Organic Acids.—W. A. Smith.—The author measures the relation between the acid strength of the first and second atoms of hydrogen in organic acids. Oswald's theory about the cause of the strength and weakness of the first and second hydrogen atoms is fully confirmed by all the results. In all comparable acids the second hydrogen atom is strong and the first weak in proportion as the hydroxyl groups are nearer to one another or further away. This is proved for acids of the oxalic series, the methyl and ethyl substituted malonic and succinic acids. For the higher homologues of the oxalic acid series the removal of two COOH groups from one another is so great that their mutual influence becomes very small.

Decomposition of some Substances under the Influence of Electric Vibrations.—Alexander von Hemptinne.—The vapour of certain substances is subjected to the action of electric vibrations and the decomposition products examined. The apparatus, of which a drawing is given, is so arranged that the vapour can be introduced at any desired pressure. The substances examined were methyl alcohol, ethyl alcohol, normal propyl alcohol, isopropyl alcohol, alkyl alcohol, propyl aldehyd, acetone, &c.

New Method of Element Change.—E. Cohen.—The determination of the temperature coefficient of the Latimer Clark cell by Callendar and Barnes shows a break in the curve at 38·75°. The stability curve for $ZnSO_4$ in water by a similar investigation shows a break at 39·7°. From the dilatometric determination of the density of zinc sulphate solution the author shows that the transformation point, between the stable and unstable phase of the salt, lies at about 38·5°.

Equilibrium in Systems of Three Components, where Two Liquid Phases can Occur.—F. A. H. Schreinmakers.—A mathematical paper unsuitable for abstraction.

Generalisation of the Observation on the Influence of Foreign Bodies on the Transformation Temperature given in the previous Paper.—H. A. Lorentz.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Ozonator.—A correspondent wishes to know where he can find particulars of the Ozonator of M. Andreoli.

MEETINGS FOR THE WEEK.

Wednesday, 15th.—Microscopical, 8. "Reports on the Foraminifera of the Malay Archipelago" (continued), by F. W. Millett. Exhibition of Sponges, by B. W. Priest.

Thursday, 16th.—Chemical, 8. Ballot for the Election of Fellows. "Preparation of a Standard Acid Solution by Direct Absorption of Hydrogen Chloride," by G. T. Moody, D.Sc. "Researches on the Terpenes—III. Halogen Derivatives of Fenchene and their Reactions," and "IV. On the Oxidation of Fenchone," by J. A. Gardner, M.A., and G. B. Cockburn, B.A.

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Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jörgensen, "Micro-Organisms and Fermentation," London (F. W. Lyon), 1893.

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Further particulars on application to the Director—

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THE CHEMICAL NEWS.

Vol. LXXVII., No. 2012.

ON THE LINDO-GLADDING METHOD OF DETERMINING POTASH.

By A. L. WINTON,
Chemist, Conn. Agricultural Experiment Station, and Reporter on Methods of Potash Determination for the Association of Official Agricultural Chemists for the Years 1896 and 1897;
and
H. J. WHEELER,
Chemist, R. I. Agricultural Experiment Station, and Reporter on Methods of Potash Determination for the Association of Official Agricultural Chemists for the Years 1894 and 1895.

(Concluded from p. 265).

Breyer and Schweitzer state that it is very "doubtful whether the method of Lindo-Gladding is a simplification of Fresenius's method." At all events, it should be stated that the members of the Association, after having given both methods an extended trial, find the latter decidedly shorter.

Breyer and Schweitzer state that potassium platinichloride obtained by them by the Lindo-Gladding method contained impurities, notably magnesium and calcium sulphates, but as they give no figures it is to be assumed that the amounts present were not determinable.

If the potash exists as chloride, and chlorides of sodium, magnesium, and calcium are the only soluble impurities, evaporation with platinum solution and washing with alcohol should yield pure potassium platinichloride, the salts of chloroplatinic acid, with the other bases, being readily soluble in alcohol. Were this not true neither the Lindo-Gladding nor the Stassfurt method would be practicable.

If, however, the bases mentioned are combined wholly or in part with sulphuric acid, the potassium platinichloride, obtained by the Lindo-Gladding method is usually, after the first washing, contaminated with magnesium and calcium sulphates; subsequent washing with ammonium chloride solution being depended upon to remove these impurities.

Magnesium sulphate is readily soluble in the ammonium chloride solution. Even when a very considerable amount is present, the first addition of the reagent removes almost instantly the greater part of it. Calcium sulphate does not dissolve so readily, but it is contained only in small amount in the potash manure salts on sale in the United States, and the treatment with ammonium chloride solution effectually removes both this salt and the magnesium sulphate.

That this is true is shown by the figures obtained by one of us (A. L. W.), which are given in Table III. The results, calculated from the weights of K_2PtCl_6 (together with many others, equally accurate, obtained by seven American chemists), were reported to the Association of Official Agricultural Chemists in 1896 (U.S. Department of Agriculture, Div. of Chemistry, *Bull.* 49, pp. 27—38), but those calculated from the weights of metallic platinum are here given for the first time.

The materials used were chemically pure potassium sulphate, which had been ignited until all water was removed, and three mixtures of salts representing the water-soluble ingredients, other than potash salt, contained in sulphate of potash (90 per cent), sulphate of potash and magnesia, and kainit. The solutions for analysis, representing half-grm. portions of the commercial potash salts named, were prepared by mixing weighed portions of the pure salt with the corresponding amounts of the mixtures of impurities, dissolved in each case in 25 c.c. of water. The determination of potash in these solutions presented the same analytical difficulties as would have been encountered in the analysis of the real commercial salts, but the exact amount of potash present was in each case known, and the results obtained could be compared with theory.

The Lindo-Gladding method of the Association (U.S. Dept. of Agric., Div. of Chem., *Bull.* 46, p. 23) was strictly followed, except in the case of the kainit solution, which was evaporated directly with platinum solution, without previous separation of lime, as was originally directed by Gladding (U.S. Dept. of Agric., Div. of Chem., *Bull.* 7, p. 41). The potassium platinichloride was weighed on Gooch crucibles, reduced in hydrogen, washed with hot water, ignited, and weighed as metallic platinum; all of which was accomplished without transfer. The small amounts of potash in the impurities were determined by careful analysis and calculated as potassium sulphate.

The conversion factors employed were:—K_2PtCl_6 to K_2SO_4, 0·3587; and Pt to K_2SO_4, 0·8937. These were derived from the following atomic weights:—Pt = 195·0, K = 39·11, Cl = 35·45, S = 32·06, O = 16·0.

The factors which have commonly been used in potash determinations (0·3056 for converting K_2PtCl_6 to KCl, 0·3570 to K_2SO_4, and 0·19308 to K_2O) are those based on an atomic weight of platinum long since abandoned. Fresenius (*Zeit. Anal. Chem.*, xxi., 238) found in some determinations made on pure potassium chloride shortly after the now-accepted atomic weight of platinum was determined by Seubert (*Ann. Chem.*, ccvii., p. 1), that the factor 0·3056 gave results nearer theory than the factor derived from the later atomic weights. But it has been shown by one of us (A. L. W., *Journ. Am. Chem. Soc.*, xvii., p. 453) that when platinum solution is added to a concentrated solution of the potash salt, as was done by Fresenius, much of the potassium platinichloride separates out at once as a finely-divided precipitate, which, examined under the microscope, may be seen to consist of radiating crystals, enclosing numerous globular cavities containing liquid. Part of the enclosed liquid is slowly driven off at 100°, more at 130°, and still more at 160° C. As Fresenius dried at 130°, the water was presumably only partially removed, and for this reason the lower factor gave the best results. Winton has further shown, however, that when the solution of the potash salt is so dilute that the addition of the platinum solution either forms no immediate precipitate, or one that dissolves on heating, the potassium platinichloride deposits slowly on evaporation in the form of coarsely granular crystals, which appear under the microscope to be almost entirely free from enclosed liquid, and which dry as completely on heating three hours at 100° as when heated for many hours at 130° and 160° C. When the salt is obtained by this latter method, as was the case in all the determinations of Tables I., II., and III., the factors based on the latest atomic weights give satisfactory results. The fact that the results (given in Table III.) obtained by the Lindo-Gladding method, and calculated by the revised factor, agree closely with those calculated from the weight of the platinum and with theory, is of itself a strong indication of the purity of the potassium platinichloride and the perfection of the process. It is only in the case of methods which yield an impure double salt that it is necessary to resort to the unscientific procedure of retaining incorrect factors in order to compensate for errors of the method.

Vogel and Haefke (*Die Landw. Versuchs-Stationen*, 1896, xlvii., pp. 115—116), as their first point against the Lindo-Gladding method, claim that the addition of sodium chloride is unnecessary, and is liable to prove a source of error. This intended criticism was made in 1896, five years after the matter was first considered by the Association, and three years after the Association had ceased to employ it—a fact which they might have ascertained had they consulted the published records of the Association.

TABLE III.—Results by the Lindo-Gladding Method on Mixtures representing Sulphate of Potash (90 per Cent), Sulphate of Potash and Magnesia, and Kainit.

Taken. Impurities corresponding to 0·5 grm. of—	Taken. K_2SO_4 pure salt.	Taken. K_2SO_4 in impurities.	Taken. K_2SO_4 total.	Found. K_2PtCl_6.	Found. Pt.	Results calculated from weight of K_2PtCl_6.		Results calculated from weight of Pt.	
						Found. K_2SO_4.	Error. K_2SO_4.	Found. K_2SO_4.	Error. K_2SO_4.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
Sulphate of potash (90 per cent) ..	0·4042	0·0002	0·4044	1·1248	0·4523	0·4035	−0·0009	0·4042	−0·0002
	0·4121	0·0002	0·4123	1·1483	0·4615	0·4119	−0·0004	0·4124	+0·0001
	0·4110	0·0002	0·4112	1·1448	0·4591	0·4106	−0·0006	0·4103	−0·0009
Sulphate of potash and magnesia ..	0·3040	0·0003	0·3043	0·8470	0·3408	0·3038	−0·0005	0·3046	+0·0003
	0·2686	0·0003	0·2689	0·7490	0·3017	0·2687	−0·0002	0·2696	+0·0007
	0·2566	0·0003	0·2569	0·7136	0·2866	0·2560	−0·0009	0·2561	−0·0008
Kainit	0·1387	0·0005	0·1392	0·3860	0·1547	0·1385	−0·0007	0·1383	−0·0009
	0·1727	0·0005	0·1732	0·4807	0·1922	0·1724	−0·0008	0·1718	−0·0014

Again, Vogel and Haefke, after calling attention to the well-known fact of the double decomposition which results when potassium platinichloride is acted upon by ammonium chloride, further add that proof is lacking to show that the ammonium chloride, even after having been brought in contact with potassium platinichloride, is not capable of effecting still further double decomposition. Assuming that such further action results to a degree which practically interferes with the accuracy of the method, they find therein another point against it. In fact, two years before this theoretical criticism was published, the Association had shown that the wash solution was capable, under greatly exaggerated conditions of treatment, of further effecting a considerable amount of double decomposition; but at the same time, as has already been shown, it was proved that in actual analytical work the amount of error thus introduced was practically so small as to furnish no valid objection to the method. Vogel and Haefke could have learned these facts also before their criticisms appeared had they consulted the published records of the Association whose official methods they were discussing. It must be conceded that, upon theoretical grounds only, many valuable and reliable methods of analysis would have to be discarded if the solvent action of the wash liquids, regardless of the degree of solubility, were the sole basis for such a procedure.

The variation in the time employed in washing the potassium platinichloride, due to unequal rapidity of filtration and the size of the crystals to be washed, are also urged by Vogel and Haefke as logical objections to the method. However, by the use of the Gooch crucible, and by precipitating the potassium platinichloride from dilute solutions (by which large crystals are obtained), it must be obvious—and, in fact, it has been shown by abundant analytical data—that these objections hold only from a theoretical, and not from a practical standpoint.

Vogel and Haefke still further assert, based upon assumption or upon the previously mentioned statements of Breyer and Schweitzer, that the potassium platinichloride obtained by the Lindo-Gladding method contains many impurities, and therefore that it is not advisable to weigh the double salt as such. However, as has been shown by the results in Table III., the potassium platinichloride, obtained by the Lindo-Gladding method, even in the presence of such impurities as are in sulphate of potash (90 per cent) and the commercial sulphate of potash and magnesia, as well as in kainit, is practically pure, and the results accord as closely as could be desired with those obtained by reduction and weighing the metallic platinum.

From what has been said above, it will be seen that Vogel and Haefke were not well informed as to the work of the Association, nor in relation to the status of the method in vogue when their unfavourable criticisms were made; furthermore, they present no analytical data of their own in support of their assumptions, and, in the main, the points which they sought to make were but a reiteration of the previous unfavourable criticisms of Breyer and Schweitzer, which have been shown by abundant data to have been, so far as practical considerations go, utterly unfounded.

THE SEPARATION AND ESTIMATION OF IODINE, CHLORINE, AND BROMINE.

By AD. CARNOT.

MANY methods have already been proposed for the estimation of these three bodies in a mixture of haloid salts. By offering still another one, I am actuated by the fact that it appears to have the qualities of simplicity, rapidity, and exactness, which cannot be found in any of the already known methods. I have used the excellent advice given by Fresenius for the estimttion of the iodine, and I also took advantage of some observations made by M. Dechan and M. Baubigny relative to bromine.

The method is founded on the following reactions. In a mixture of chlorides, bromides, and iodides in solution, sulphuric acid charged with nitrous vapours entirely displaces iodine in the cold, without acting on hydrochloric or hydrobromic acid in any manner whatever; the iodine can thus be entirely dissolved and removed by sulphide of carbon. On adding sulphuric and chromic acids the bromine is isolated very slowly in the cold, but by heating up to about 100° for from half an hour to an hour, it can be entirely isolated, by dissolving in sulphide of carbon on cooling; no trace of chlorine is set at liberty in one case or the other. The estimation of this body can then be made by means of nitrate of silver.

The free iodine is estimated volumetrically by hyposulphite of sodium, added to the sulphide of carbon until exact decolouration takes place; for bromine the operation is similar, but iodide of potassium must be first added, after which the violet colour given by the free iodine must be exactly neutralised by means of titrated hyposulphite of sodium.

A series of experiments carried out on the most varied proportions of chloride, bromide, and iodide have proved the trustworthiness of the results when the necessary precautions are taken.

1. *Iodine*,—The neutral solution of the salts, diluted to about 200 cubic centimetres, is placed in a spherical funnel of from 350 to 400 c.c. capacity, well plugged at the upper part by a ground stopper, and at the lower extremity by a glass tap made of sufficiently thin glass that there will be no risk of breakage on heating. Into the cold solution ten drops of sulphuric acid saturated with nitrous vapours (produced by the reaction of concentrated nitric acid on starch) are poured, after which 10 to 15 c.c.

Proportions used in the experiments.						Hyposulphite used for the—		AgCl	Element found.		
Iodide. M.grms.	Bromide. M.grms.	Chloride. M.grms.	I. M.grms.	Br. M.grms.	Cl. M.grms.	I. C.c.	Br. C.c.	weighed. M.grms.	I. M.grms.	Br. M.grms.	Cl. M.grms.
200	100	200	153·0	67·2	95·2	22·3	15·2	380	152·5	65·3	94·0
100	100	100	76·5	67·2	47·6	11·2	15·4	—	76·6	66·2	—
100	200	100	76·5	134·4	47·6	11·2	31·0	192	76 6	133·3	47·5
20	40	200	15·3	26·9	95·2	2·2	6·3	—	15·0	27·1	—
5	50	200	3·8	33·6	95·2	0·6	7·8	—	4·1	33·5	—
1	100	600	0·8	67·2	285·6	0·1	15·3	—	0·7	65·8	—
—	20	500	—	13·4	238·0	—	3·1	—	—	13·3	—
—	10	200	—	6·7	95·2	—	1·5	—	—	6·4	—
—	5	200	—	3·4	95·2	—	0·7	—	—	3·0	—
—	1	200	—	0·7	95·2	—	0·1	—	—	0·4	—
100	100	20	76·5	67·2	9·5	11·2	15·5	39	76·6	66·6	9·6
100	100	5	76·5	67·2	2·4	11·2	15·6	10	76·6	67·1	2·5

of pure sulphide of carbon is introduced. The glass stopper is firmly fixed and the apparatus thoroughly shaken several times; the sulphide of carbon is then allowed to collect, while the bulb is carefully rotated to collect the small drops of sulphide which adhere to the surface of the glass. If there is much iodine present the sulphide of carbon will now be of a deep violet colour, or if, on the other hand, there is only a small quantity, the colour will be of a pale rose tint; this is easily seen in the aqueous solution, and it also fills the lower part of the bulb and the fine tube down to the stopcock.

The stopcock is then carefully turned, and the sulphide of carbon run on to a filter previously moistened with water; the tap must be quickly turned off the moment the aqueous solution is about to pass. Another 10 c.c. of sulphide of carbon is then added and the whole shaken as before; as a rule there is now very little colouration by iodine; four or five drops of nitrous sulphuric acid are again added, and after further agitation there should be no change of colour if the first operation has been properly carried out. The solution is now allowed to settle again, and the sulphide is collected on the same filter, which must be covered by a clock-glass to prevent evaporation.

The addition of two or three cubic centimetres of sulphide of carbon and one or two drops of nitrous sulphuric acid will serve to collect the small droplets which still remain on the surface of the solution; this also assures one of the complete displacement of the iodine, besides serving to wash out the small quantity of faintly coloured sulphide still remaining in the stopcock.

The sulphide of carbon which has been collected on the moistened filter must then be well washed with cold water. The first washings only are collected and added to the aqueous solution in the glass bulb for the purpose of analysis. By piercing the filter the sulphide of carbon can be run into a small ground-stoppered bottle, in which is about 30 c.c. of a half per cent of bicarbonate of soda. To this mixture is then added, by means of a graduated burette, a titrated solution of hyposulphite of sodium (either decinormal or centinormal) until the complete decolouration of the sulphide of carbon. The solution must be well shaken after each addition of the reducing agent. The reaction is very distinct, and the results are as accurate as possible, not only in the presence of chlorides, as was observed by Fresenius, but also in the presence of bromides.

2. *Bromine.*—For the estimation of bromine a few c.c. of chromic acid at 10 per cent and three or four c.c. of sulphuric acid diluted with its own volume of water are added to the contents of the funnel, which must now be firmly closed and placed in a hot water bath for at least an hour. It is then allowed to cool completely, after which sulphide of carbon is added and the operation completed in the same manner as has just been described in the case of iodine, by three successive exhaustions. The sulphide of carbon is then received on a moistened filter, and washed with cold water until the latter is no longer acid.

The sulphide is then run into a ground glass stoppered flask, to which a small quantity of iodide of potassium and about 30 c.c. of bicarbonate of sodium is added. The flask must now be well shaken several times. The bromine displaces an equivalent quantity of iodine, which, when set free, gives on dissolution a violet colour to the liquid, of a much stronger character than the yellowish brown tint caused by the original bromine. The estimation of the iodine is made as before, by titrating with hyposulphite of sodium, and to arrive at the corresponding weight of bromine we have simply to multiply the weight of iodine by 80/127.

3. *Chlorine.*—The acid solution, from which the iodine and bromine has been removed, and to which the first wash-waters have been added, must now be poured into a beaker and diluted with about 500 c.c. of water; nitrate of silver is then added and the solution heated to collect the chloride. The precipitate will be slightly coloured by the presence of a small quantity of chromate of silver; to purify it the filtrate must be decanted after cooling, and the volume made up by warm water slightly acidulated with nitric acid; this is once more allowed to cool and is then washed by decantation. The chloride of silver, which should now be perfectly white, is collected on a tared filter, dried, and weighed with the usual precautions.

This estimation of the chlorine is, of the three, the one to which, as a rule, the least importance may be attached. As a matter of fact, instead of estimating directly, as I have just described, it would generally be quite sufficient to estimate by difference; this can easily and rapidly be done volumetrically in the following manner. The determination should be carried out on the solution, from which the iodine has already been removed by the first operation. This must be divided into two portions; the first is only used for the estimation of the bromine, as has just been described; the other is precipitated by a measured quantity of titrated nitrate of silver; the excess of silver is then estimated by means of sulphocyanide, using ferric iron as indicator; according to the quantity of the bromine found the amount of nitrate of silver used is known, and thus the chlorine is calculated.

We can also, especially if the chlorides are present in much greater quantity than the bromides and iodides, take only 1/10th or 1/50th of the original neutral solution, add chromate of potassium to it as indicator, and then, by means of a graduated burette, run in titrated nitrate of silver until the red colour of the chromate appears. By deducting from the nitrate of silver used the amount which corresponds to the iodine and to the bromine, we get the quantity which was precipitated by the chlorine.

The chlorine can thus be very easily estimated by either of these methods.

The accompanying table, showing the results of a series of trials carried out on either very large or very small proportions of each of these three bodies, enables us to appreciate the accuracy which can generally be attained by this method.

For a simple *qualitative research* for small quantities of iodides or bromides in the presence of a large excess of

an alkaline chloride, we recommend the following manner of working:—

1. Separate the iodine in a small quantity of the neutral solution by nitrous-sulphuric acid, and collect it in a few drops of sulphide of carbon. The violet or rose colouration is extremely sensitive.

2. The iodine having been eliminated, add to the liquid, placed in a small flask, a little chromic and sulphuric acids; then heat to boiling, while keeping the flask covered with yellow fluoresceine paper, as described by M. Baubigny, who pointed out its sensitiveness to bromine. The very smallest quantities of bromine will be revealed by the characteristic rose-colour.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 6.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 10th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 2nd to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined by us, all were found to be clear, bright, and well filtered.

For the first time this year we have to record an excess of rain at Oxford. The actual fall during the month of May was 2·33 inches, the average fall during the last thirty years is 1·83 inches, we thus have an excess for the month of 0·5 inch; this reduces the deficiency for the year to 2·57 inches.

Our bacteriological examinations of 241 samples have given the results recorded in the following table; we have also examined 41 other samples, from special wells, standpipes, &c., making a total of 282 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	227
New River, filtered (mean of 24 samples) ..	8
Thames, unfiltered (mean of 25 samples) ..	1473
Thames water, from the clear water wells of five Thames-derived supplies (mean of 120 samples)	23
Ditto ditto .. .. highest	578
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	7693
River Lea, from the East London Company's clear water well (mean of 24 samples) . ..	25

On the 16th of the month one sample was found to give abnormally bad results. The affected Company's Engineer was immediately telephoned to, and we were informed that a defect had been found in one of the filters, and this defect was being rectified when the Engineer received our message. The quality of the water was soon improved, and has since remained good.

The increase of rainfall has made itself apparent on our results, both chemical and bacteriological, but only to a slight extent; the water remaining in a very satisfactory condition.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

ON THE CONDITION OF OXIDATION OF MANGANESE PRECIPITATED BY THE CHLORATE PROCESS.*

By F. A. GOOCH and MARTHA AUSTIN.

(Concluded from p. 270).

CONFINING our attention to the last two simpler iodometric methods—the reduction of the higher oxide by an acidified iodide on the one hand and by arsenious acid on the other—we made, first, some experiments to determine the accuracy with which manganese may be thus estimated. We used for the manganese compound of known oxidising power a solution of potassium permanganate filtered carefully through asbestos and standardised against ammonium oxalate which had been found to be the exact equivalent of a specially-prepared lead oxalate. For each experiment a definite portion of this solution was drawn from a burette and treated with a solution of pure manganous sulphate until the colour of the permanganate had vanished, thus precipitating a hydrous oxide approximating quite closely probably to the condition of oxidation of the dioxide, but containing at all events, whatever its actual composition might be, the exact amount of available oxygen originally in the permanganate. In the experiments of the following table this precipitate was treated with a solution of potassium iodide (6 grms.) and tartaric acid (10 grms.), by which the freshly-prepared hydrate is dissolved quite as well as by the iodide and hydrochloric acid of Pickering's original method and with less risk of evolution of iodine outside the main reaction. From the iodine found by titration with this sulphate we have calculated the weight of manganese dioxide which would liberate it; and a comparison of this value with the amount of the dioxide theoretically precipitated by the interaction of the known permanganate and the sulphate, upon the assumption that two molecules of the former throw down five molecules of the hydrated dioxide, should disclose the error of the analytical process when applied to the estimation of manganese dioxide. In all probability the assumption that it is the dioxide that is precipitated, and which afterwards acts upon the iodide, is not quite true under the conditions, since the precipitation takes place in presence of an excess of a manganous salt; but for our purpose it does not matter, since we are in effect simply dealing with the oxidising power of a known amount of permanganate.

Thus, it is obvious that the mean error of the results is practically inconsiderable, varying between extremes of −0·0004 grm. and +0·0007 on 0·1351 grm. of manganese dioxide.

In the experiments of Table III. the precipitated oxide was treated with an excess of a standard arsenious acid solution and 5 c.m.³ of sulphuric acid of half strength, and the whole was heated until the manganese dioxide was dissolved. To this liquid was added tartaric acid (10 grms.) to prevent the precipitation of the manganese and

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science* Vol. v., p. 260.

the oxidation by iodine in the subsequent titration, the acid was neutralised by acid potassium carbonate, and the arsenic still remaining in the arsenious condition titrated by standard iodine.

TABLE II.

Mn theoretically precipitated by $KMnO_4$ as MnO_2. Grm.	Mn in MnO_2 corresponding to iodine found. Grm.	Error of the analytical process (applied to MnO_2) in terms of Mn. Grm.
0·1351	0·1347	0·0004 –
0·1351	0·1347	0·0004 –
0·1351	0·1350	0·0001 –
0·1351	0·1353	0·0002 +
0·1351	0·1358	0·0007 +
0·1351	0·1353	0·0002 +

TABLE III.

Mn precipitated by action of $KMnO_4$ on $MnSO_4$ as MnO_2. Grm.	Mn in MnO_2 corresponding to As_2O_3 oxidised. Grm.	Error of the process in terms of Mn. Grm.
0·1392	0·1396	0·0004 –
0·1109	0·1117	0·0008 –
0·1112	0·1117	0·0005 –
0·1109	0·1117	0·0008 –
0·1109	0·1117	0·0008 –
0·1117	0·1125	0·0008 –

It is clear that either of these methods of reduction, the action of an acidified iodide or that of arsenious acid, is capable of yielding fairly accurate indications when we have to deal with a pure salt of manganese. When, however, the manganese is associated with a considerable amount of iron, as is frequently the case, it becomes a matter of necessity to separate the manganese before attempting its estimation. For this purpose, the "chlorate process" is by far the simplest of those generally used, and though it has been the subject of much discussion it is at present the method of separation most widely used by the practical chemists, whether the final estimation of the manganese is made gravimetrically, as in Ford's process, or volumetrically, as in the methods of Volhard, Williams, or Pattinson.

Definite portions of the solution of pure manganous chloride were drawn from a burette into an Erlenmeyer flask of 300 c.c. capacity, evaporated to dryness, precipitated by the "chlorate process" with the modifications given in detail above. The oxide, after careful washing, was returned with the asbestos to the flask, and treated by one or other of the methods to be described. It was either treated with potassium iodide (5 grms.) and sulphuric acid (10 c.c.) of half strength, the iodine set free being estimated by thiosulphate; or it was heated with an excess of standard arsenious acid and 10 c.c. of sulphuric acid of half strength, and, after cooling, adding 5 grms. of the Rochelle salt and neutralising with acid potassium carbonate, the arsenious acid remaining unoxidised was estimated with standard iodine. In Table IV. are given the results obtained from this work.

The results show plainly that, while the manganese is so completely precipitated in the chlorate process of oxidation when properly conducted that only insignificant traces may escape, the condition of oxidation cannot be taken to be that of the dioxide. The average error thus put upon the determination of the manganese known to be present is more than 2 per cent. It follows, as a matter of course, that the indications of any process which rests upon the assumption that the oxygen value of the manganese compound precipitated in the chlorate process corresponds to that of the dioxide must of necessity be erroneous. If, therefore, the chlorate method is to be employed for the separation of the manganese, it is obvious that precautions must be taken to secure a definite condition of oxidation of the manganese before processes which depend upon the oxygen value of the higher oxide may be applied for the estimation of that element. The process which in our hands seems to give the oxide in

TABLE IV.

Mn taken in the form of manganous chloride. Grm.	Mn found upon the hypothesis that MnO_2 is precipitated. Grm.	Error. Grm.	Mn found in the filtrate after evaporation and treatment with bromine and ammonia. Grm.
	By Reduction with Potassium Iodide.		
0·1225	0·1183	0·0042 –	0·00006
0·1225	0·1177	0·0048 –	Trace
0·1225	0·1180	0·0045 –	0·00008
0·1225	0·1169	0·0056 –	Trace
	By Reduction with Arsenious Acid.		
0·1222	0·1189	0·0033 –	Not determined.
0·1222	0·1191	0·0031 –	,, ,,
0·1222	0·1199	0·0023 –	,, ,,
0·1222	0·1200	0·0022 –	,, ,,
0·1222	0·1186	0·0036 –	None
0·1222	0·1187	0·0035 –	0·0001
0·1222	0·1189	0·0033 –	0·0002
0·1222	0·1194	0·0028 –	Trace
0·1222	0·1205	0·0017 –	0·0001

definite condition is based upon the observations of Wright and Menke (*Journ. Chem. Soc.*, xxxvii., 36) that a dilute solution of potassium permanganate acting in excess, at 80° C., in the presence of zinc sulphate, and in thorough mixture upon manganous sulphate, yields an oxide which, though combined with alkali, holds the oxygen exactly in the proportion corresponding to the dioxide. Three-fifths of the manganese in such a precipitate represents the amount of that element originally present in the manganous salt. In the following table are given the results of experiments in which manganese was determined iodometrically after the interpolation of the permanganate treatment.

In these experiments a solution of manganous chloride of known strength was drawn from a burette, evaporated to dryness in a small beaker, heated with nitric acid until there was no evidence of the presence of nitrogen oxides. Strong nitric adid was poured in until the volume was 85 c.m.^{3}, sodium chlorate (5 grms.) was added carefully, the liquid was boiled five minutes, more nitric acid (15 c.m.^{3}) and a few crystals of the chlorate were introduced, and the solution brought to boiling temperature again. After cooling, the liquid was filtered on asbestos and washed with water, and the oxide upon the asbestos and walls of the beaker was dissolved in 2 c.m.^{3} of hydrochloric acid. After diluting a little, the solution was evaporated with 5 c.m.^{3} of strong sulphuric acid until no more hydrochloric acid remained. The solution of manganous sulphate (not exceeding 0·5 grm. of the salt), very nearly neutralised by potassium carbonate, was mixed with a solution of zinc sulphate (2 grms.) and a freshly and carefully filtered dilute solution of potassium permanganate (1·5 grm. of the salt); the liquid, amounting now to about 500 c.m.^{3}, was heated to 80° C. and acid potassium carbonate added, in quantity a little more than enough to neutralise the remnant of the acid present. The precipitate was collected upon asbestos, and after careful washing was returned to the flask in which the precipitation had been made. The oxygen value of the oxide was determined by one or other of the methods described. In the one case the flask was fitted with a paraffined stopper having two bores, one holding a Will and Varrentrap absorption apparatus (in which a solution of potassium iodide dissolved any escaping iodine), the other a small separating funnel. Sulphuric acid and potassium iodide in solution were run in through the funnel, the iodine set free was titrated with thiosulphate—the amount of manganese being reckoned from the iodine set free. The results of this work follow in the first part of Table V. In the second case the dioxide obtained in the manner described above was reduced by warming gently with a decinormal solution of arsenious acid. After cooling, and neutralising with acid potassium carbonate in the presence

of Rochelle salt, the excess of the arsenious acid was estimated with iodine in the presence of starch. The estimation by this method gave the results recorded in the second part of Table V.

TABLE V.

Mn taken in the form of chloride. Grm.	Mn found upon the hypothesis that MnO_2 is the oxide finally obtained. Grm.	Error. Grm.
By Reduction with Potassium Iodide.		
0·0643	0·0637	0·0006 –
0·0643	0·0642	0·0001 –
0·0643	0·0642	0·0001 –
0·0651	0·0651	0·0000
0·1125	0·1121	0·0004 –
0·1125	0·1121	0·0004 –
0·1125	0·1120	0·0005 –
0·1214	0·1206	0·0008 –
0·1214	0·1207	0·0007 –
0·1214	0·1223	0·0009 +
0·1214	0·1214	0·0000
By Reduction with Arsenious Oxide.		
0·1213	0·1212	0·0001 –
0·1213	0·1201	0·0012 –
0·1213	0·1203	0·0010 –
0·1213	0·1208	0·0005 –

These results show plainly that if the precautions to which attention has been directed are taken, viz., dilution of the solution and heating to 80° C., presence of zinc sulphate, and (most essential of all) the almost complete neutralisation of free acid before the addition of the potassium permanganate, the manganese dioxide precipitated by the chlorate process from pure manganous nitrate may subsequently, after reduction, be brought by the permanganate treatment so nearly to the full degree of oxidation represented by the symbol MnO_2, that the amount of manganese originally treated may be calculated with a very fair degree of accuracy from the oxygen value of three-fifths of the oxide found. We do not recommend this procedure as a rapid analytical method; our purpose is accomplished when the fact is brought plainly to view that the oxide precipitated by the chlorate process is not the dioxide, but that it may be made such by subsequent treatment.

A DETERMINATION OF THE ATOMIC WEIGHT OF PRASEODYMIUM AND OF NEODYMIUM.*

By HARRY C. JONES.

THE determinations of the atomic weight of the supposed element didymium have been discussed, to a greater or less extent, by Meyer and Seubert ("Atomgewichte," 218), Ostwald ("Lehrb., Allgem. Chem.," i., 70), and Clarke ("A Re-calculation of the Atomic Weights," 351—353). Yet, for the sake of completeness and reference, a brief account of what has been done will be given here.

Marignac (*Ann. Chim. Phys.* [3], xxvii., 231; xxxviii., 151) precipitated the sulphuric acid from a solution of didymium sulphate by means of barium chloride, but found that when the precipitate was boiled, in the presence of even a large excess of the chloride, it still contained didymium sulphate. His best results were obtained by precipitating the didymium from a solution of the sulphate, as oxalate, by means of oxalic acid, and decomposing the oxalate at a very high temperature, to avoid the presence of superoxide. He found, as the mean of five determinations, 143·58 (SO_3=80) as the atomic weight of didymium.

Hermann (*J. Prakt. Chem.*, lxxxii., 387) precipitated the didymium from a solution of the sulphate, as oxalate, by means of ammonium oxalate, decomposed the oxalate by heat, and weighed the oxide. He found 146·7 for the atomic weight of the element. The determination of the chlorine in the chloride gave 142·2 as the atomic weight of didymium. Zschiesche (*J. Prakt. Chem.*, cvii., 75) decomposed the sulphate to the oxide, and obtained the value 141·8. Erk (*Ztschr. Anal. Chem.*, x., 509), using the method of Hermann, found the atomic weight of didymium to be 142·35. He also precipitated the sulphuric acid from the solution, out of which the didymium had been separated by oxalic acid, as barium sulphate. By this method the atomic weight was found to be 142·29. He employed, in addition, the method which Marignac first used, precipitating the sulphuric acid directly from a hydrochloric acid solution of didymium sulphate, as barium sulphate, and obtained the figure 143·46. This is necessarily erroneous, since, as Marignac has pointed out, some didymium sulphate is always carried down under these conditions.

Hillebrand (*Ann. der Phys. Pogg.*, clviii., 71) converted a weighed amount of the metal into the nitrate, and then into the oxide, and found 144·78 (O=16) as the atomic weight of didymium. By the aid of the Bunsen ice calorimeter he found that the specific heat of pure metallic didymium was 0·04563. This number multiplied by 144·78 gives 6·60, which agrees with the law of Dulong and Petit. This shows that the atomic weight of didymium must be expressed by a number very nearly of the order of that given above, and not by two-thirds of this amount. Therefore didymium forms the normal sesquioxide Di_2O_3, and not DiO.

Clève (*Bull. Soc. Chim.*, xxi., 246) heated the oxide in a stream of hydrogen to remove all superoxide, and from the sesquioxide thus obtained he synthesised the sulphate. As a mean of six determinations he obtained the value 147·01, maximum 147·23, minimum 146·65.

The presence of samarium was later discovered in the above material. This was removed (*Ibid.*, xxxix., 289), and ten new syntheses of the sulphate effected from the pure sesquioxide. The mean of these new results is 142·33, maximum 142·49, minimum 142·03.

Brauner (*Ber. der Chem. Ges.*, xv., 109; *Monatsh. Chem.*, iii., 14) effected the synthesis of the sulphate from the oxide, and, as the mean of three determinations, obtained the value 146·58.

Later (*Monatsh. Chem.*, iii., 499; *J. Chem. Soc.*, xliii., 278) he made five determinations with samples prepared in different ways, and found as a mean 145·42, with a difference between the highest and lowest value of 0·22. While these results agree fairly well with one another, they differ about a unit from his earlier result, which makes it probable that the oxide first employed contained some element of higher atomic weight. He tested this point as follows:—

Some of the didymium oxide used in the first series of experiments, which gave 146·58 as the atomic weight of the element, was fractionally precipitated with ammonia. The atomic weight of didymium, as determined with the fraction which was precipitated last, was found to be 145·40, which made it more probable that the substance first used contained an element with higher atomic weight. Further fractionation confirmed this point beyond question. Brauner concluded that the atomic weight of didymium was probably 145·2 to 145·4.

Bauer ("Inaugural Dissertation," Freiburg, 1884) synthesised the sulphate from the oxide, and obtained, as a mean of four determinations, the value 142·74.

Auer von Welsbach (*Monatsh. Chem.*, vi., 477) showed that didymium is not an element, but is composed of at least two, thereby invalidating all the preceding results, without, however, affecting the value of the methods which had been used. He effected the separation by

* From the *American Chemical Journal*, vol. xx., No. 5.

fractional crystallisation of the double nitrate of ammonium and didymium, from strong nitric acid, and repeating the process several thousand times. The one element forms green salts and green solutions, and the other rose-coloured solutions, and the salts are the colour of amethyst. To the former he gave the name *praseodymium*, and to the latter *neodymium*. Both the emission and absorption spectra of the two elements are different, but their sum is the same as the corresponding spectrum of didymium.

The elements resemble one another more closely than in any other known cases. Their conduct towards oxygen is, however, very different. Neodymium forms only the sesquioxide Nd_2O_3, while praseodymium forms most readily the oxide Pr_4O_7; indeed this is formed whenever the oxalate, or sesquioxide, is heated in contact with air. It is easily reduced to the sesquioxide in a stream of hydrogen gas. Von Welsbach, without giving any details or even the method employed, assigned the atomic weight 143·6 to praseodymium, and 140·8 to neodymium.

Later, Crookes (*Nature*, xxxiv., 266) stated that, "although I have not split up didymium into the two earths, or groups of earths, which are described by Dr. Auer, other processes of fractionation gave me, so to speak, other cleavage planes, or lines of scission, through the compound molecule, didymium. . . . . Neodymium and praseodymium must not be considered as actual chemical elements, but only the names given to two groups of molecules, into which the complex molecule didymium splits up, by one particular kind of fractionation."

The material used in carrying out the piece of work about to be described was furnished me, with unusual generosity, by Mr. Waldron Shapleigh, of the Welsbach Light Company, Gloucester, New Jersey, who has also made many valuable suggestions in connection with the separation of the elements. I wish to state here that this work was made possible only by the abundance of the comparatively pure praseodymium and neodymium compounds which Mr. Shapleigh placed at my disposal.

The Atomic Weight of Praseodymium.

About 1¼ kilos. of the double nitrate of praseodymium and ammonium were furnished me by Mr. Shapleigh. It was analysed spectroscopically by means of the large Rowland spectroscope, with a concave grating of about 21 feet local length, by Dr. W. J. Humphreys, and found to contain small amounts of neodymium, cerium, and lanthanum. No trace of any of the other rare elements, whose presence might reasonably be expected, could be detected.

The double nitrate, which had been thus far purified, was treated as follows:—The entire mass was dissolved in water containing a little nitric acid, and evaporated until crystals appeared. The solution was then cooled until a part of the double nitrate separated. This was filtered from the solution, and, since it contained more of the lanthanum, was discarded. The solution was then strongly acidified with nitric acid, and evaporated on the water-bath until, on cooling, about two-thirds of the total material crystallised out. This was the purest praseodymium, and was used for further crystallisation. The mother-liquor was filtered from these crystals and discarded, because it was richest in neodymium. The original substance was thus separated by fractional crystallisation into three parts, the first and last being discarded, and the second preserved as the purest material. The second portion was then treated exactly as the original substance, being separated into three portions by fractional crystallisation, and the middle portion again treated in the same manner. This process was repeated twenty-one times. Any impurities, such as calcium, iron, &c., were separated from the middle fraction of the last crystallisation, by precipitating the praseodymium with oxalic acid, in the presence of nitric acid. Only praseodymium oxalate is thrown down under these conditions. The oxalic acid used was purified by repeated crystallisation from a mixture of alcohol and ether, to remove acid salts, and contained no detectable trace of either potassium or sodium. The water used in dissolving the praseodymium salt, also in washing the oxalate, and in all the processes of crystallisation, had been especially purified by distilling, first from acid permanganate, and then from alkaline, in the apparatus described by myself and Mackay (*Amer. Chem. Journ.*, xix., 91; *Zeitschr. Phys. Chem.*, xxii., 237). In all of this work the solutions were never allowed to come in contact with glass vessels while warm, but only with porcelain.

The precipitation of the oxalate was effected by pouring very slowly the hot dilute solution of the double nitrate of praseodymium and ammonium into a hot dilute solution of oxalic acid, with vigorous stirring. The oxalate thus precipitated separated in a form which could be easily washed free from impurities. A portion of this oxalate was subjected to spectrum analysis, and was found to contain a trace of neodymium, cerium, and lanthanum. The amount of the neodymium present was determined by comparing the intensity of the absorption bands of the neodymium in a solution of the praseodymium salt of known concentration, with the absorption bands of the neodymium salt, also of known concentration. A very concentrated solution of the double nitrate of praseodymium and ammonium was prepared, and the intensity of the absorption bands of neodymium noted. Then the solution of the double nitrate of neodymium and ammonium was diluted until the absorption bands were of the same intensity of those of the neodymium in the praseodymium salt. The amount of the neodymium in the solution of the neodymium salt was known, since this was prepared of standard concentration. The amount of the neodymium in the praseodymium salt could thus be calculated directly. By comparing the intensity of the absorption bands of neodymium in the two solutions, by bringing first the one and then the other into the field of the Steinheil spectroscope, we could estimate very closely the amount of the neodymium present in the praseodymium salt. It was found to be 0·06 per cent, and could therefore be disregarded.

A further attempt was made to remove the trace of cerium and lanthanum, since the exact amounts present could not be determined accurately, because of the absence of sufficiently intense absorption bands. The oxalate of praseodymium, purified as just described, was decomposed by heat into the oxide, in a platinum vessel. The oxide was dissolved in nitric acid, the excess of acid evaporated, and the solution of the nitrate poured into a large volume of pure boiling water. The cerium present would then be precipitated as the basic nitrate, and a slight cloudiness in the solution was observed. This was repeated until the solution, in a large volume of water, was perfectly clear.

The solution of praseodymium nitrate was evaporated, and enough purified ammonium nitrate added to form the double salt. The double nitrate was then crystallised from a very strong nitric acid solution, far stronger than had been hitherto used, in order to remove the remaining trace of lanthanum. This was repeated several times.

The solution of the double nitrate of praseodymium and ammonium, thus purified, was poured into oxalic acid, after being acidulated with nitric acid, as before described, to remove any calcium, iron, &c., which might have gotten in during the separation of the traces of cerium and lanthanum. The oxalate was washed with the greatest care, converted into the oxide, and this again analysed spectroscopically by Mr. L. E. Jewell. No trace of cerium was detected, and only a trace of lanthanum.

This oxide, which was used in the following determinations, was blackish brown, and had the general properties of a superoxide. When dissolved in sulphuric acid there was a copious evolution of oxygen.

It was easily reduced to the sesquioxide when heated in a stream of hydrogen gas. When the superoxide was reduced to the sesquioxide it lost 2·5 per cent of oxygen, corresponding closely to the composition Pr_4O_7, which is the composition of the superoxide described by Von Welsbach (*Monatsh. Chem.*, vi., 489). It is thus quite clear that the superoxide of praseodymium which I employed, agreed in all its essential properties with that isolated and used by Von Welsbach.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 2nd, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. A. L. H. Garside and K. J. P. Orton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Walter Birkett, 23, Cheviot Street, Lincoln; Alfred Hartridge, 14, Broad Street, Oxford; Charles William Tuthill Woods, St. Kilda, Tudor Road, Upper Norwood.

The Death of Lord Playfair.

The President said that the melancholy duty devolved on him to announce the death of the Right Hon. Lord Playfair, P.C., G.C.B., LL.D., F.R.S., the senior Past President and last surviving Founder of the Society, which took place on Sunday, May 29th. It was needless for him to dwell on Lord Playfair's scientific standing, or well recognised position in public life; he would only refer to the fact that he was the creator of a new type of public servant, and his services to education and as a member of Royal and Departmental Commissions on subjects connected with the public welfare were so unquestioned that it would be well for the country if there were more such men. Lord Playfair was ever ready to acknowledge his indebtedness to Liebig, Graham, and his other teachers, and proud to attribute his successful career to his early training in scientific method as a chemist. The Society would be represented at the funeral at St. Andrews by a former President, Professor Crum Brown, F.R.S.

In consequence of the death of Lord Playfair, the Banquet to the Past Presidents, arranged for June 9th, had been postponed until Friday, October 28th.

The following papers were read:—

83. "*The Boiling-point and Density of Liquid Hydrogen.*" By James Dewar, LL.D., F.R.S.

The boiling-point of liquid hydrogen at atmospheric pressure has been determined by a platinum resistance thermometer. This was constructed of pure metal and had a resistance of 5·3 ohms at 0° C., which fell to about 0·1 ohm. when the thermometer was immersed in liquid hydrogen. On reduction of this resistance to normal air temperatures, the boiling-point is found to be −238·2° and −238·9° respectively by two methods, and to be −237° by a Dickson formula calculated for this thermometer (*cf. Phil. Mag.*, 1898, xlv., 525). The boiling-point of the liquid is, therefore, about −238° C. or 35° absolute, and is thus about 5° higher than that obtained by Olszewski by the adiabatic expansion of the compressed gas, and about 8° higher than that deduced by Wroblewski from van der Waals' equation. It may be inferred that the critical point of hydrogen is about 50° absolute, and that the critical pressure will probably not exceed 15 atmospheres. As molecular latent heats are proportional to absolute boiling-points, the latent heat of liquid hydrogen will be about two-fifths that of liquid oxygen. From analogy, it is probable that the practicable lowering of temperature to be obtained by evaporating liquid hydrogen under pressures of a few m.m. cannot amount to more than 10—12° C., and it may be said with certainty that no means are at present known for approaching nearer than 20—25° to the absolute zero of temperature. The platinum resistance thermometer used had a zero point of −263·2 platinum degrees, and when immersed in boiling liquid hydrogen indicated a temperature of −256·8° on the same scale, or 6·4 platinum degrees from the point at which the metal would become a perfect conductor. The effect of cooling platinum from the boiling-point of liquid oxygen to that of liquid hydrogen is to diminish its resistance to one-eleventh.

The approximate density of liquid hydrogen at its boiling-point was determined by measuring the volume of the gas obtained by evaporating 10 c.c., and is slightly less than 0·07, or about one-sixth that of liquid marsh gas, which has a density of 0·41, and is the lightest liquid at its boiling-point hitherto known. It is remarkable that, with so low a density, liquid hydrogen is so easily seen, has so well-defined a meniscus, and can be so readily collected and manipulated in vacuum vessels. As hydrogen occluded in palladium has a density of 0·62, it follows that it must be associated with the metal in some other state than that of liquefaction. The atomic volume of liquid hydrogen at the boiling-point is about 14·3, the atomic volumes of liquid oxygen and nitrogen being 13·7 and 16·6 respectively at their boiling-points. The density of the gas at the boiling-point of liquid hydrogen is 0·55, or about one-half that of air, and is eight times that of the gas at ordinary temperatures. The ratio of the density of hydrogen gas at the boiling-point to that of the liquid is approximately 1 : 100, as compared with a ratio of 1 : 255 in the case of oxygen.

The specific heat of hydrogen in the gaseous state and in hydrogenised palladium is 3·4, but may very probably be 6·4 in the liquid substance. Such a liquid would be unique in its properties; but as the volume of 1 grm. of liquid hydrogen is about 14—15 c.c., the specific heat per unit volume must be nearly 0·5, which is about that of liquid air. It is highly probable, therefore, that the remarkable properties of liquid hydrogen predicted by theory will prove to be susceptible of explanation when they are compared with those of liquid air, volume for volume, at corresponding temperatures as defined by van der Waals.

84. "*The Action of Hydrogen Bromide in presence of Ether on Carbohydrates and certain Organic Acids.*" By Henry J. Horstman Fenton, M.A., and Mildred Gostling, B.Sc.

It has been previously shown by one of the authors (*Trans.*, 1896, lxvii., 553) that ethylic dihydroxymaleate can be readily produced by the interaction of the acid with anhydrous ether in presence of hydrogen bromide. This behaviour of ether as a "base" being unusual, at any rate, towards organic acids, it was considered desirable to make experiments with other acids in a similar manner; the results indicate that the reaction is a general one, and that the yields are satisfactory.

The study of the behaviour of ether and hydrogen bromide is now being extended to substances other than acids, and an account is given of the results obtained with carbohydrates and allied polyhydric alcohols. Certain of these substances develop an intense purple colouration, and it is found that the presence of ether, although advantageous, is not essential for its production. The coloured substance seems to resemble the compound described by Stenhouse and others as "metafurfurol." So far as the investigation has proceeded, ketohexoses and carbohydrates such as inulin, which yield them on hydrolysis, give an intense purple colouration in the course of an hour or two; aldohexoses give a purple colouration of comparatively moderate intensity in the course of a day or two; and other carbohydrates, such as arabinose, rhamnose, starch, and cellulose, and alcohols such as mannitol, dulcitol, and glycerol, give a brown, red, or

yellow colouration free from any shade of purple. The only exception to this classification yet met with is xylose, which, although in the purest state obtainable, behaves similarly to the ketohexoses.

Discussion.

Mr. Chapman asked whether the authors had made any experiments with hydrogen chloride. Bouillon-Lagrange and Vogel (*Annales de Chimie*, 1809, lxxi., 91) had stated that both cane-sugar and milk-sugar absorb hydrogen chloride, forming coloured products, which evolve the gas with effervescence on treatment with sulphuric acid.

Mr. Fenton, in reply, said that hydrogen chloride gives only a slight red colour, even after long standing, and that hydrogen iodide acts as a reducing agent liberating iodine.

85. "*Production of some Chloropyridinecarboxylic Acids.*" By J. N. Collie, Ph.D., F.R.S., and W. Lean.

The authors have prepared from ethylic chlorolutidinecarboxylate (*Trans.*, 1897, lxxi., 303) several chloropyridinecarboxylic acids, and, by reducing one of them with tin and hydrochloric acid, carbocinchomeronic acid, which is also one of the products of the action of oxidising agents on quinine, and several other alkaloids.

Ethylic chlorolutidinemonocarboxylate was prepared by the action of phosphorus pentachloride on ethylic oxylutidine carboxylate. It is a sweet-smelling liquid, boiling at 288—290°. *Chlorolutidinecarboxylic acid* can be obtained by hydrolysis of the ethylic salt; it crystallises in small needles, melting at 148°. By the action of potassium permanganate on the ethylic salt, two acids were obtained, one having the formula—

$$C_5HN(CO_2H)_2(CO_2Et)Cl, \ (\alpha\gamma : \beta : \alpha'),$$

and melting at 169°, the second being an *α'-chloropyridine-αβγ-tricarboxylic acid*, $C_5HN(CO_2H)_3Cl$, melting at 212°. The latter acid yielded carbocinchomeronic or pyridine, αβγ-tricarboxylic acid, $C_5H_2N(CO_2H)_3$, when reduced with tin and hydrochloric acid.

PHYSICAL SOCIETY.

Ordinary Meeting, June 10th, 1898.

Mr. Shelford Bidwell, President, in the Chair.

Dr. S. P. Thompson described and exhibited a model illustrating Max Meyer's theory of Audition. Max Meyer abandons the audition theory of Helmholtz, and contends that analysis takes place in the ear otherwise than by resonance of the Corti organ. Imagine a jointed system, like a hand, to be oscillated from one end, *i.e.*, from the finger-tips. A small motion affects only the top joints, but a large motion affects the whole structure. Such a structure is the membrane of the inner-ear. It widens towards one end, and is effectively damped by the contained liquid. Wave-motions of different amplitudes run along it to different distances before they are extinguished; these distances are recorded by nerves, and are thereby communicated to the Corti organ. In the model the compound-wave to be analysed is cut out on the edge of a disc of zinc, so that, as the disc revolves, the motions are communicated to a frame-work. If the frame is thus moved through more than a certain distance, a displacement occurs which sets a second frame in motion, and so on to a third and fourth. The depth to which the motion penetrates is indicated by a series of glow-lamps connected electrically to the frames.

Prof. Ayrton said it had for some time past occurred to him, when considering the way in which an expert telegraph clerk reads syphon-recorder signals on a long cable, that it might be possible to analyse waves without the supposition of a resonating apparatus. The clerk interprets not so much the motions to one side or other of the zero-line as the rate of change of velocity, *i.e.*, the acceleration of the syphon. This had been recognised in the design of those relays for long cables, where the lever makes contact when the received current exceeds a certain value, and breaks contact when the current falls below a certain minimum. Messrs. Siemens had adopted a relay in which the lever was carried on the suspended coil of a d'Arsonval galvanometer by a pivot with a small amount of friction. If contact was made, the coil could, nevertheless, continue its motion in a given direction. If that direction altered, contact was immediately broken, and the lever passed over to the opposite stop, thereby reversing the local circuit. It was possible that, in the process of hearing, something akin to this took place, the ear behaving as a mechanism responsive, not by resonance to to the complete waves, but by its sensitiveness to changes of direction of the received impulses.

Dr. S. P. Thompson thought that a mechanism similar to the relay described by Prof. Ayrton was contained in the telautograph of Elisha Gray; it was a "Prony" mechanism. In the acoustical problem the ear was probably sensitive to abrupt changes of shape in the waves as well as to reversals. In the case of mistuned octaves, something is heard that suggests "revolving" in the ear, indicating a cyclic change. In this regard it was necessary to take into account the phase-relations as well as the relative intensities of the component tones.

Mr. E. H. Barton then read a paper on the "*Attenuation of Electric Waves along a Line of Negligible Leakage.*"

It forms a sequel to a paper communicated to the Physical Society and printed in their *Proceedings* of December, 1897, and January, 1898. Shortly after the publication of the earlier results, Mr. Oliver Heaviside drew attention to Lord Rayleigh's high-frequency formula for the "Effective Resistance" of wires to alternating currents, and suggested that the formula might be approximately applicable to the case; but he thought the experimental value of the attenuation would be considerably higher than the one derived from calculations. Mr. Barton here repeats the work, with special precautions as to the mode of insulating the parallel copper wires through which the wave-train proceeds. The value of the attenuation-constant deduced from these experiments is 0·000013. By applying Lord Rayleigh's formula for the effective resistance of the circuit, and using this value in Mr. Heaviside's expression for the attenuation, the calculated constant is 0·000006 2. To account for the discrepancy, the author points out that the effective resistance formula was originally developed for a wire placed at a considerable distance from other parts of the circuit, and for currents following the harmonic law. Whereas, in the experiments the conditions are—(1) wires 1·5 m.m. diameter, only 8 c.m. apart, and (2) the waves are propagated in the form of a damped train, with the large end leading; they are extinguished after ten or a dozen vibrations.

Mr. Oliver Heaviside (communicated) pointed out that, as there was human interest in error, it might be worth mentioning that at first it was supposed the previous experiments of Dr. Barton made the index of the attenuation-factor to be six times that of the long-wave theory for simple periodic waves. And it was hard to account for so large a discrepancy. The discovery of an error in the figures reduced the result from six to two. The small depth of the surface-layer of effective conduction, and the distance apart of the wires, seemed now to make it improbable that E. Barton's first reason, (1), was adequate to account for the doubling of resistances. The second, (2), was of course a substantial reason for increased resistance. A third one, Mr. Heaviside suggested, was the external resistance at the boundary of the waves. A combination of the second and third reasons, with a little of the first, might account for most of the extra attenuation observed, and, if more was wanted, one could "*try the K. R. law.*"

Mr. Appleyard said it was rather to be regretted that, in all the experiments, the distance between the wires had been the same, *i.e.*, 8 c.m. By taking a few different values (1) might have been checked. Lord Rayleigh's formula for the effective resistance involved the square-root of the magnetic permeability of the wires. The author had, throughout, used copper, a paramagnetic metal, and had assumed $\mu=1$. It would be of advantage to try other metals.

Mr. Barton, in reply, said he would make further experiments with the two conductors at different distances apart, and he would also try iron wires. With iron, the thickness of the surface-layer of the effective conductor was about one-thirteenth that of copper. Iron should therefore give a greater value of the attenuation than copper.

Mr. A. Griffiths then read a paper on "*Diffusive Convection*,"—a phenomenon analogous to caloric convection.

The differences of density that produce convection-currents are not due to changes of temperature, but to variations in the quantity of dissolved substance per unit volume. The author has devised an apparatus consisting of a vessel divided horizontally by a diaphragm, through which pass two vertical tubes of unequal lengths. A solution of copper sulphate, maintained at constant strength, is placed in the lower compartment. The upper compartment is filled with water. Diffusion takes place up the tubes. One tube is 4 c.m. long, the other is 4·05 c.m. The tops of the tubes are exactly at the same level. Up the longer tube, and down the shorter, diffusive convection occurs at the rate of 5 c.m. per year. This flow *increases* the quantity of copper sulphate transmitted by the long tube by about 2 per cent, and *diminishes* that transmitted by the shorter tube by about the same amount. Consequently, the resultant increase due to the motion is only a fraction of 1 per cent. To detect the flow the author employs a second piece of apparatus, in which the upper ends of the tubes are separated by a capillary, containing coloured liquid. By this means the motion is considerably magnified.

Dr. S. P. Thompson asked whether, in a case where a large tube was used in determining the velocity, the viscosity of the liquid would not play a very much less part than with narrow tubes.

Mr. Griffiths explained that viscosity was not important until very small tubes were considered, *e.g.*, those of the order 0·001 m.m. diameter.

The President proposed votes of thanks to the authors, and to Dr. Max Meyer, for lending the Society his model. The meeting then adjourned until June 24th.

CORRESPONDENCE.

GAS AND GASES.

To the Editor of the Chemical News.

Sir,—Attentive examination of the statement made to the Royal Society, by Prof. Ramsay, at the meeting of June 9th, shows that, instead of establishing a new element, he has disestablished one already accepted. It is obvious that the residual gas obtained from the atmosphere, by repeating the classical experiment of Cavendish, is a mixture of argon and krypton in unknown proportions. It is equally obvious that the residual gas obtained from the evaporation of the last few cubic centimetres of a quantity of liquid air is a mixture of the same gases, again in unknown proportions. The first may be presumed to contain more argon than krypton, and the second more krypton than argon; but that is all that can be said with any degree of certainty.

Professor Ramsay talks of disentangling the spectra of these two gases, by the simple process of assigning to krypton the lines that do not belong to argon. But as he has never isolated argon he does not know what lines belong to it and what lines to the admixture of krypton. He is simply comparing two mixtures in different proportions, but in neither case in known proportions, one of which at least must be of variable composition. In such circumstances it is evident that argon and krypton are mere names, connoting no scientific entity whatever. For anything Professor Ramsay knows, what he now calls krypton may be a mixture, just as he has proved that what he called argon is a mixture. Indeed it is practically certain that a third gas is present in the Cavendish residue, because some gas not yet named has been escaping for centuries from the Bath springs along with nitrogen and helium.

Now, Sir, I submit that to claim the discovery of new elements on such grounds as these is not science. If a man is to be hailed as the discoverer of a new element merely because, from a mixture which he has not analysed, he obtained a spectroscopic line or lines not yet assigned to a known element, then Liveing and Dewar discovered krypton four years ago, and Dewar discovered last November an element to which he has not given a name. Cavendish proved, more than a century ago, that the air contains something which is neither oxygen, nitrogen, nor carbonic acid. Except that the spectroscope proves this something to be more complex than Cavendish would probably have supposed it, or that Professor Ramsay supposed it when he announced it to be argon, I am totally at a loss to see what addition of accurate scientific knowledge has been made to what Cavendish proved.—I am, &c.,

Suum Cuique.

NOTICES OF BOOKS.

Optical Activity of Organic Substances, and its Applications. ("Das Optische Drehungsvermögen Organischer Substanzen und dessen Praktische Auwendungen.") By Dr. H. Landolt, Professor of Chemistry in the University of Berlin. Second Edition, completely Revised. Pp. 655. Brunswick. 1898.

Since the first edition of this work, in 1879, the interest of chemists in the subject of "optical activity" of organic substances has received a great stimulus from the acceptation of the theory of the asymmetric carbon atom—a theory which at that time was receiving the first confirmations of practical experiment.

From the time that van 't Hoff and Le Bel pointed out the now undoubted relationship between optical activity and atomic constitution in organic compounds, the records of research in this branch of chemistry have accumulated to bewildering proportions.

To reduce to order a mass of literature covering a period of nearly twenty years' work on this subject was by no means an easy task. That the author has been completely successful must be the opinion of all chemists who read the book, and who are interested in the subject upon which it bears.

To the practical worker the book will be invaluable, methods of investigation being admirably described, and details of manipulation completely given.

For convenience the book is divided into six parts. The first part is devoted to the general considerations of optical activity. The history of the subject is briefly touched upon; then come "Classification of Active Bodies," "Nature of Optical Activity," "Relationship between Optical Activity and Chemical Constitution of Organic Substances," and "Optical Modifications." This last chapter of Part I. gives a very complete account of the more important optical isomers, with tabulated details

of their relative densities, physiological action, solubility, &c.

The second part gives an account of the Laws of Circular Polarisation, and the third part treats of the numerical values for the optical activity of substances under varying conditions (*e.g.*, when crystalline, and in concentrated and dilute solutions), and of the influence of solvents, &c.

The fourth part gives details of apparatus and methods for the determination of Specific Rotation. The fifth part treats of the "Practical Applications of Optical Activity," the subject of saccharimetry receiving special attention.

Part the sixth, and last, gives a *resumé* of the numerical values so far found for the rotatory power of optically active bodies.

The theories bearing on the subject of the work are clearly and concisely stated. The tables throughout will save endless reference, and must have cost a vast amount of labour and care. We strongly recommend the book to all serious students of chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 17, April 25, 1898.

Industrial Treatment of the Emerald by the Electric Furnace.—B. Lebeau.—If this mineral is heated in a carbon tube in the electric furnace for eight or ten minutes with a current of 950 ampères and 45 volts, the greater part of the silica distils off, and there remains a melted mass having a metallic lustre; this consists of a mixture of carbide of aluminium, carbide of glucinum, silicide of iron, and silicide of carbon. It is attacked by dilute acids, giving a solution containing glucina and alumina. By using hydrofluoric acid a fairly pure solution of fluoride of glucinum can be obtained at once, fluoride of aluminium being insoluble. If half its weight of carbon is added to the emerald a complete reduction is soon arrived at; the silica is completely eliminated either by volatilisation or by the formation of silicide of carbon, a body almost as unassailable as diamond. Some of these experiments were carried out on 100 kilos. of emerald.

On the Quinonoximes.—A. Valeur.—The quinones form two kinds of oximes, the mono-oximes, and the di-oximes. The first may be obtained by the action of chlorhydrate of hydroxylamine on the quinones in alcoholic solution, or by the action of nitrous acid on the phenols; the quinonoximes are, in fact, identical with the nitrosophenols. In this paper the author gives the results of his examination of the monoximes of ordinary quinone, of thymoquinone, and of the naphthoquinones. He has measured the heat of combustion of a certain number of these compounds, and finds a constant difference between the heat of combustion of these oximes and the corresponding quinones of about 60 cals.

On the Products from the Splitting-up of Ouabaine by Hydrolysis.—M. Arnaud.—Boiling dilute hydrochloric and sulphuric acids hydrolyse ouabaine completely, though slowly. The splitting-up is first shown by the cloudy appearance of the liquid, which becomes milky, and finally gives a rapidly increasing deposit of a deep yellow resinous matter. The hydrolysis is generally done on 20 grms. of crystallised hydrated ouabaine, $C_{30}H_{40}O_{12}.9H_2O$, dissolved in twelve times its weight of water acidulated with two per cent of H_2SO_4, heated in a sealed tube at 100° for forty or fifty hours. The clear liquid, separated from the melted residue, is neutralised with baryta. The estimation of the reducing sugar is made by means of Fehling's solution, and compared with a typical solution of pure rhamnose. It is found that 21·10 to 21·80 per cent of anhydrous rhamnose, $C_6H_{10}O_3$, corresponds to the hydrated ouabaine; the identity of these two bodies has been established. The resin has not been obtained in crystals; it is easily soluble in concentrated alcohol, methyl alcohol, ether, &c. To obtain it in the anhydrous state it must be heated to above its melting point, 130°—135°, away from contact with air, as it is very readily oxidisable when warmed. The splitting-up of ouabaine is expressed thus:—

$$C_{30}H_{40}O_{12} + H_2O = C_6H_{12}O_3 + C_{24}H_{36}O_8.$$

Chloridising Action of Ferric Chloride in the Aromatic Series.—V. Thomas.—The reduction of ferric chloride by benzene commences at the ordinary temperature; though the quantity of hydrochloric acid set free in the cold is small, the reduction is more rapid when the temperature is raised, and at 80° it is very energetic. When this action is ended the residue is exhausted with boiling benzene and distilled; between 130° and 134° a colourless liquid comes over—this is monochlorobenzene. This is not the extent of the action; by starting with more or less chloridised benzenes (mono-, di-, tri-, &c.) the whole series up to the hexachloride can be obtained. A similar reaction takes place with the toluene.

The Phosphoric Di-Ethers.—J. Cavalier.—The author has shown that when phosphoric acid, PO_4H_3, passes to the state of mono-ether, PO_4RH_2, it is the acidity of the weakest which disappears. The results here show that the same is the case when a new radical, R, is introduced, when passing from PO_4RH_2 to the di-alcoholic acid, PO_4R_2H. The acid function which persists is comparable with the most energetic of the acid functions of the mono-alcoholic acid and the phosphoric acid.

The Acid Phosphoglycerates.—MM. Adrian and Trillat.—The acid phosphoglycerates can be prepared by decomposing the corresponding neutral salts by the theoretical amount of sulphuric acid, in the presence of helianthine as an indicator, or by the double decomposition between the acid salt of barium and a soluble sulphate. The acid phosphoglycerates are distinguished from the neutral salts by their great solubility in water. They are difficultly precipitable from their solutions by alcohol, which even at 50° dissolves a considerable proportion. They do not crystallise, and when dried *in vacuo* they appear in the form of a white vitreous mass (blue in the case of the copper salt), unchangeable at 100°. On the other hand their aqueous solutions are decomposed on boiling, forming free phosphoric acid and glycerin.

MISCELLANEOUS.

The Kekulé Memorial.—We desire to recall the attention of our readers to the Kekulé Memorial Fund, as to which an announcement appeared in our columns on February 25th last (Chem. News, vol. lxxvii., p. 88), and to urge any who intend to subscribe to send in their contributions without delay to Dr. Hugo Müller, 13, Park Square East, N.W., as we understand that the Committee propose shortly to close the account.

Paris Exhibition of 1900.—The Royal Commission are now prepared to circulate information respecting the Exhibition. The classification and rules for Exhibitors, together with forms of application for space, can be obtained by applying to the Secretary of the Royal Commission, Paris Exhibition 1900, St. Stephen's House, Westminster, S.W.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on Monday afternoon (the 6th inst.), Sir James Crichton-Browne,

M.D., F.R.S., Treasurer and Vice-President, presiding. The following was elected a Member:—Mr. A. W. Horsburgh. The special thanks of the Members were returned for the following donations to the fund for the promotion of Experimental Research at Low Temperatures:—Mrs. G. J. Romanes, £5; Sir Frederick Bramwell, £100; Professor Dewar, £100; Dr. Ludwig Mond, £200; Charles Hawksley, Esq., £100; Sir David Salomons, Bart., £21; Dr. Rudolph Messel, £100.

Investigation of Crystalline Liquids.—R. Schenck.—The author proves that liquid crystals correspond, not only in their optical, but also in their whole behaviour, to solid crystals. In liquid crystals there is a changing point, which in all cases expresses a melting point. He examines the behaviour of the liquids *p*-azoxyanisol, *p*-azoxyphenetol, and cholesteryl benzoate, by estimating the surface energy at various temperatures, from measurements of the density of the isotropic and anisotropic phases of the liquid.—*Zeit. fur Physikalische Chemie*, xxv., No. 2.

An International Competition for the invention of a paste containing no white phosphorus, to be used in the manufacture of matches, is being organised by the Belgian Government. A prize of £2000 is offered to the successful competitor. The following are some of the conditions governing the competition:—The paste must offer such resistance to shocks and friction that dangerous explosions need not be feared during manufacture, and it must not contain any material which may be dangerous to the health of the operatives. The matches must be capable of igniting when rubbed on various substances, even on cloth, and must be able to withstand various alterations of moisture and dryness, heat and cold, within certain limits, without deterioration; they must not be spontaneously inflammable or decomposable. Inventors will be admitted to the competition until January 1st, 1899. The successful inventor must be able to furnish proof that the manufacture of his matches is commercially possible, and must engage to manufacture at least one million matches on Belgian territory in the presence of the Commissioners or their delegates. Further particulars of the competition can be obtained from M. Woeste, Ministère de l'Industrie et du Travail, 2, Rue Laterale, Brussels.

On Gaïacyl.—C. Andrê.—It is well known that local anæsthesia can be produced by means of gaïacol in subcutaneous injections, and the author determined to try the effect of gaïacyl,—that is, the calcium derivative of gaïacyl-sulphurous acid, $(C_7H_7O_2,SO_3)Ca$, in collaboration with Dr. O'Folloinel. He (the author) placed 100 grms. of pure gaïacol in a matras, and gently heated it; when liquid he added very gradually 100 grms. of pure concentrated sulphuric acid, and left it at the ordinary temperature for 48 hours. It was then diluted with six or seven times its weight of distilled water, and saturated with carbonate of lime in small pieces, at 80° on the water-bath; it was then filtered and evaporated to dryness, and taken up in four or five times its weight of alcohol at 90°: this separates out a small quantity of insoluble substances. After re-evaporation and pulverisation a greyish mauve powder is left, very soluble in water and alcohol, but not in oil; this is gaïacyl. For anæsthesia 1/10th to 1/20th solutions of gaïacyl in water were used; they gave practically the same results. In extracting teeth, out of thirty-two cases, in twenty-two the anæsthesia was sufficient, in seven it was incomplete, and twice there was no effect—one case was doubtful. Out of eleven small surgical operations, in five the anæsthesia was complete, five times it was sufficient, and once it failed; that is to say, 90 per cent of success.—*Journ. de Pharm. et de Chemie*, Series 6, vol. vii., No. 7.

Synthesis of Terebic Acid.—E. E. Blaise.—The author has obtained 10 to 15 grms. per cent of terebic acid by the condensation of bromosuccinate of ethyl in an equimolecular mixture with acetone, to which an equal weight of bromised ether was added.—*Bull. Soc. Chim. de Paris.*

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Ozonator.—I notice in your last issue that a correspondent wishes to know where he can find particulars of my ozoniaers. He may write or call at the Electric Ozone Syndicate, Ld., 5, New Union Street, Moorgate St. Station, E.C.—E. ANDREOLI.

MEETINGS FOR THE WEEK.

WEDNESDAY, 22nd.—Institution of Mining and Metallurgy, 8. "The Treatment of Broken Hill Complex Sulphide Ores by Wet Extraction Processes and the Electrolytic Deposition of Zinc," by Edgar A. Ashcroft, M.Inst.M.M. "Notes on the Payable Conglomerate Beds encased in Sandstone, and the Mining Methods in use for their extraction on the Witwatersrand," by A. F. Crosse, M.Inst.M.M. "Density of Gold and Silver Alloys," by George Attwood, M.Inst.M.M.

FRIDAY, 24th.—Physical, 5. Exhibition of an Apparatus illustrating the Action of Two Coupled Electric Motors by Prof. Carus-Wilson. Exhibition of Weedon's Expansion of Solids Apparatus by Mr. J. Quick. "Theory of the Hall Effect in a Binary Electrolyte," by F. G. Donnan, M.A., Ph.D.

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GEO. MELLOR,
Secretary.

Offices of the School,
Suffolk Street,
June 6th, 1898.

THE CHEMICAL NEWS.

Vol. LXXVII., No. 2013.

ON A NEW CONSTITUENT OF ATMOSPHERIC AIR.*

By WILLIAM RAMSAY, F.R.S. and MORRIS W. TRAVERS.

This preliminary note is intended to give a very brief account of experiments which have been carried out during the past year of attempts to ascertain whether, in addition to nitrogen, oxygen, and argon, there are any gases in air which have escaped observation owing to their being present in very minute quantity. In collaboration with Miss Emily Aston we have found that the nitride of magnesium, resulting from the absorption of nitrogen from atmospheric air, on treatment with water yields only a trace of gas; that gas is hydrogen, and arises from a small quantity of metallic magnesium unconverted into nitride. That the ammonia produced on treatment with water is pure has already been proved by the fact that Lord Rayleigh found that the nitrogen obtained from it had the normal density. The magnesia, resulting from the nitride, yields only a trace of soluble matter to water, and that consists wholly of hydroxide and carbonate. So far, then, the results have been negative.

Recently, however, owing to the kindness of Dr. W. Hampson, we have been furnished with about 750 c.c. of liquid air, and, on allowing all but 10 c.c. to evaporate away slowly, and collecting the gas from that small residue in a gas-holder, we obtained, after removal of oxygen with metallic copper, and nitrogen with a mixture of pure lime and magnesium dust, followed by exposure to electric sparks in presence of oxygen and caustic soda, 26·2 c.c. of a gas, showing the argon spectrum feebly, and, in addition, a spectrum which has, we believe, not been seen before.

We have not yet succeeded in disentangling the new spectrum completely from the argon spectrum, but it is characterised by two very brilliant lines, one almost identical in position with D_3, and almost rivalling it in brilliancy. Measurements made by Mr. E. C. C. Baly, with a grating of 14,438 lines to the inch, gave the following numbers, *all four lines being in the field at once*:—

D_1	5895·0
D_2	5889·0
D_3	5875·9
D_4	5867·7

There is also a green line, comparable with the green helium line in intensity, of wave-length 5568·8, and a somewhat weaker green, the wave-length of which is 5560·6.

In order to determine as far as possible which lines belong to the argon spectrum, and which to the new gas, both spectra were examined at the same time with the grating, the first order being employed. The lines which were absent, or very feeble, in argon, have been ascribed to the new gas. Owing to their feeble intensity, the measurements of the wave-lengths which follow must not be credited with the same degree of accuracy as the three already given, but the first three digits may be taken as substantially correct:—

Violet	4317	Blue	4834
,, ...	4387	,, ...	4909
,, ...	4461	Green	5560·6
,, ...	4671	,, ...	5568·8
Blue	4736	Yellow ..	5829
,, ...	4807	,, ...	5867·7
,, ...	4830	Orange ..	6011

* A Paper read before the Royal Society, June 9th, 1898.

Mr. Baly has kindly undertaken to make a study of the spectrum, which will be published when complete. The figures already given, however, suffice to characterise the gas as a new one.

The approximate density of the gas was determined by weighing it in a bulb of 32·321 c.c. capacity, under a pressure of 521·85 m.m., and at a temperature of 15·95°. The weight of this quantity was 0·04213 grm. This implies a density of 22·47, that of oxygen being taken as 16. A second determination, after sparking for four hours with oxygen in presence of soda, was made in the same bulb; the pressure was 523·7 m.m., and the temperature was 16·45°. The weight was 0·04228 grm., which implies the density 22·51.

The wave-length of sound was determined in the gas by the method described in the "Argon" paper. The data are:—

	i.	ii.	iii.
Wave-length in air ..	34·17	34·30	34·57
,, ,, gas..	29·87	30·13	

Calculating by the formula,—

$$\lambda^2_{air} \times \text{density}_{air} : \lambda^2_{gas} \times \text{density}_{gas} :: \gamma_{air} : \gamma_{gas},$$

$$(34·33)^2 \times 14·479 : (30)^2 \times 22·47 :: 1·408 : 1·666,$$

it is seen that, like argon and helium, the new gas is monatomic, and therefore an element.

From what has preceded, it may be concluded that the atmosphere contains a hitherto undiscovered gas with a characteristic spectrum, heavier than argon, and less volatile than nitrogen, oxygen, and argon; the ratio of its specific heats would lead to the inference that it is monatomic, and therefore an element. If this conclusion turns out to be well substantiated, we propose to call it "krypton" or "hidden." Its symbol would then be Kr.

It is, of course, impossible to state positively what position in the periodic table this new constituent of our atmosphere will occupy. The number 22·51 must be taken as a minimum density. If we may hazard a conjecture, it is that krypton will turn out to have the density 40, with a corresponding atomic weight 80, and will be found to belong to the helium series, as is, indeed, rendered probable by its withstanding the action of red-hot magnesium and calcium on the one hand, and on the other of oxygen in presence of caustic soda, under the influence of electric sparks. We shall procure a larger supply of the gas, and endeavour to separate it more completely from argon by fractional distillation.

It may be remarked in passing that Messrs Kayser and Friedländer, who supposed that they had observed D_3 in the argon of the atmosphere, have probably been misled by the close proximity of the brilliant yellow line of krypton to the helium line.

On the assumption of the truth of Dr. Johnstone Stoney's hypothesis that gases of a higher density than ammonia will be found in our atmosphere, it is by no means improbable that a gas lighter than nitrogen will also be found in air. We have already spent several months in preparation for a search for it, and will be able to state ere long whether the supposition is well founded.

NOTE ON THE ESTIMATION OF ROSIN AND ROSIN OIL IN LINSEED OIL.

By L. de KONINGH, F.I.C., F.C.S.

The excellent method devised by Parker C. McIlhiney (*J. Amer. Chem. Soc.*, xvi., 275—278) for the detection of the adulteration of boiled linseed oil has not been so universally adopted as it deserves; this is, no doubt, caused by the fact that it does not distinguish between rosin and rosin oil.

By combining this process—for the details and figures of which the original paper should be consulted—with

the method for extracting unsaponifiable oils from soapy solutions by means of light petroleum, a very good assay for the purity of linseed oil is at disposal.

Samples of rosin oil used in this country for the adulteration of linseed oil were found by the writer to contain not more than 5 per cent of saponifiable matter, but Fahrion (*Zeit. Angew. Chem.*, 1898, 270) has come across a sample containing nearly 20 per cent of the same. Linseed oil adulterated with such a sample will, therefore, appear to contain added rosin as well.

The writer's process is, then, very shortly as follows:—The bromine-acidity figure of the sample is taken. If the amount of unsaponifiable matter comes to about 5 per cent, and betrays the presence of rosin oil by its odour, its bromine-acidity figure is also taken. It does not do to liberate the acids from the extracted soap-ley, and then to take their bromine-acidity number; then, even when free from rosin, they will often give an acidity figure high enough to account for 5 per cent of this substance. The writer believes that this may be accounted for by the water of hydration. McIlhiney warns against the presence of free moisture; if this causes acidity, might not the combined water act still more energetically?

If the original sample gives only a slight acidity, this may be caused by the presence of free fatty acids, but a strong bromine-acidity may be put down to joint rosin-oil and rosin, part of which, however, may be derived from the rosin oil supposing any of the latter is found in the unsaponifiable matter. Actually added rosin is generally added as a metallic resinate, so if there is no ash the presence of true rosin becomes very doubtful.

The writer has had no opportunity of taking the bromine-acidity figure of such samples as mentioned by Fahrion, after alkali treatment; investigation in this respect is highly desirable.

4, St. Martin's Road, Stockwell, S.W.,
June 8, 1898.

SPECTRAL RESEARCH ON ATMOSPHERIC AIR.

By MM. MOISSAN and DESLANDRES.

At the meeting of the French Academy on the 15th of June last MM. Moissan and Deslandres asked for a sealed packet, deposited by them on May 11th, 1896, to be opened. This packet was numbered 5213, and was duly opened by the President. It contained the following note:—

During the course of researches undertaken on the gases given off by the mineral cerite, when heated *in vacuo*, we have carefully studied, by spectroscopic means, the residue left by these gases, after explosion with oxygen in the eudiometer and absorption of the excess of oxygen by means of pyrogallic acid.

The residue, (1 or 2 c.c.) was introduced into a vacuum tube connected with a mercury pump, fitted with drying tubes filled with caustic potash and anhydrous phosphoric acid.

Now the spectrum of the residue, examined principally in the blue and the violet, showed the characteristic bands of nitrogen fairly strongly, the helium lines, some of the argon lines, and, further, the following lines, which have not yet been ascribed to any known gas:—

Intensities counted from 1 to 10, 10 being the strongest.	Wave-lengths.
7	415·17
3	414·37
4	411·00
4	410·80
2	410·05

In this experiment the gas from the cerite and the oxygen were present in about equal quantities; but the residue obtained with oxygen only, also gave the new lines more or less strongly, even when the oxygen had been prepared from chlorate of potash, permanganate of potash, and native binoxide of manganese.

However, the characteristic lines of nitrogen were always present; and as nitrogen was, to a certain extent, supplied by the use of the mercury oven, it was thought that atmospheric air might be playing a *rôle*, and so ordinary air was introduced into the same sparking-tube, and the spectra examined at diminishing pressures.

Now these new lines were still apparent, but only at a certain pressure, less than 1 m.m., and below the pressure of maximum brightness of the nitrogen tubes. At this same pressure the characteristic lines of argon would also be seen, though faintly, the line λ 415·87 being the most prominent.

The new lines appeared stronger when the air was replaced by nitrogen obtained from nitrite of ammonium, or separated from ordinary air by the usual pyrogallic acid method, the protochloride of chromium method, or by copper at a red heat.

On the other hand, the lines disappeared at the same time as those of nitrogen, when the nitrogen was absorbed by lithium or by magnesium. But still, these new lines might be strictly attributed to impurities, to vapours emitted, or to the matter actually forming the rarefied tube,—such as glass, metallic electrodes, mercury, grease, potash, phosphoric acid; but their relative intensity does not increase when the pressure gradually diminishes, as is the case with the mercury lines. Further, they have been obtained in spectrum tubes of crystal and of German glass, with and without metallic electrodes; they have been observed without the characteristic cyanogen bands, which form a very delicate test in the simultaneous presence of carbon and of nitrogen; they have again been persistent after the introduction of oxygen which caused the disappearance of all the mercury lines. Finally, they were missing in the gases which had been absorbed by potash and heated in the vacuum tube with either phosphoric acid or red or white phosphorus.

It may be concluded that these are either nitrogen lines due to low pressure and not yet noted, or that they are due to a new gas existing in the atmosphere, closely resembling nitrogen in its chemical properties. The simultaneous appearance of the argon lines render the latter alternative most probable.—*Comptes Rendus*, cxxvi., No. 24, June 15, 1898.

ON THE PREPARATION AND PROPERTIES OF ANHYDROUS FLUORIDE OF GLUCINUM AND OF OXYFLUORIDE OF GLUCINUM.

By P. LEBEAU.

Berzelius showed that a fluoride of glucinum could be prepared by the action of hydrofluoric acid on hydrate of glucinum. He described this compound as a body soluble in water in all proportions, drying to a colourless transparent mass, remaining limpid up to +60°, but losing its water at 100° and becoming milky; at a higher temperature the substance becomes puffed up, and half melts like alum. Heated to redness it loses a part of its hydrofluoric acid if the desiccation has not been complete, but the residue from the calcination still dissolves in water, giving a clear solution.

We have taken up the study of this reaction, and have endeavoured to determine whether the product obtained was really anhydrous fluoride of glucinum or not. To this end, pure hydrated glucina was dissolved in pure hydrofluoric acid quite free from silica, and the clear solution was evaporated on a water-bath in a platinum dish. The liquid becomes concentrated into a gummy mass, which we were able, however, to bring to a powdery form by constant stirring. This substance, dried as perfectly

as possible at 100°, is not anhydrous fluoride of glucinum: the product, which is besides very deliquescent, always retains water; its proportion of glucinum never exceeds 17 per cent.

We next calcined the residue at different temperatures varying from 440° to 800°. In contact with air we observed the same phenomena as those described by Berzelius, viz., partial fusion, puffing, and complete solution in water.

Analysis showed that the substance heated to redness has a practically constant composition, corresponding to an oxyfluoride of the formula $5GlF_2,2GlO$:—

	I.	II.	III.	Theory for $5GlF_2,2GlO$.
Glucinum ..	22·01	23·31	22·90	22·26
Fluorine.. ..	66·97	65·92	66·12	66·54
Oxygen (by dif.)	11·02	10·77	10·98	11·20

These analyses were made on three different samples.

The oxyfluoride is an almost transparent white body, completely soluble in water. The density at 15° is about 2·01.

Thus it is shown that anhydrous fluoride of glucinum cannot be obtained by the desiccation of the residue from the evaporation of a hydrated solution of fluoride of glucinum.

We next tried the evaporation and desiccation in a current of hydrofluoric acid gas. To effect this the substance, almost completely dried over the water-bath, was placed in a platinum boat which was in turn placed in a tube of the same metal; this tube was traversed by a regular current of hydrofluoric acid gas.

The temperature of the platinum tube was slowly and regularly raised to a bright red. After cooling, a melted transparent substance was found in the platinum boat closely resembling glass, but very deliquescent, the composition of which is that of a fluoride of glucinum, GlF_2. There was also a ring of the same composition formed round the boat; it consisted of a melted vitreous part and a pulverulent deposit of small crystals. The analysis of this compound gave the following results:—

	Found.			Calculated for GlF_2.
Glucinum ..	19·03	19·41	19·52	19·28
Fluorine ..	80·90	80·04	80·33	80·72
	99·93	99·45	99·85	100·00

We have identified this fluoride as being the same as that we prepared by the reaction of fluorine or of hydrofluoric acid gas on carbide of glucinum.

These methods for the formation of fluoride of glucinum only enabled us to prepare a small quantity of that substance; we therefore set to work to try and find a more practical method.

M. Camille Poulenc (*Ann. de Chim. et de Phys.*, Series 7, vol. ii.), in his researches on anhydrous fluorides, often made use of the calcination of ammoniacal fluorides. By this means he was enabled to obtain, starting from an ammoniacal salt, an anhydrous fluoride, sometimes amorphous and sometimes crystallised. We hoped to apply this method to the preparation of fluoride of glucinum. The double salt $GlF_2,2(NH_4)F$, studied by Marignac (*Ann. de Chim. et de Phys.*, Series 4, vol. xxx., p. 47) is easily obtained crystallised, and can be dried perfectly. This salt, decomposed in a current of carbonic acid gas in a platinum vessel almost hermetically sealed, gave us an anhydrous fluoride of glucinum.

Properties of Anhydrous Fluoride of Glucinum.—Anhydrous fluoride of glycinum is found in the form of a vitreous transparent mass, or as a sublimate consisting of very deliquescent small crystals:—D = 2·1 at 15°.

The fluoride melts in a similar manner to glass, taking a pasty condition, but it becomes very fluid towards 800°. It is notably volatile at this temperature, giving a deposit of white crystals.

Fluoride of glucinum dissolves in water in all proportions. It is also slightly soluble in absolute alcohol, and very soluble in alcohol at 90°. By cooling an alcoholic solution to −23° a white mass of crystalline texture is formed; this melts very rapidly as soon as the temperature is raised. Etherised alcohol also acts as a solvent.

Most of the metalloids are without action on fluoride of glucinum. Oxygen transforms it into oxyfluoride; the vapour of sulphur has no effect whatever up to the temperature of the softening of glass.

Fluoride of glucinum is attacked by sulphuric acid. It forms an anhydrous sulphate and hydrofluoric acid. We have not succeeded in dissolving fluoride of glucinum in anhydrous hydrofluoric acid. By throwing the fluoride into the liquefied acid, there is no sensible rise in temperature. This experiment shows that the existence of an acid fluoride of glucinum is very improbable.

Fluoride of glucinum is reduced by sodium at a red heat, with the formation of fluoride of sodium, while metallic glucinum is set at liberty. The difficulty in fusing the fluoride and its hygroscopic properties cause this salt to be very inconvenient for the easy preparation of the pure metal. With potassium the reaction is much more energetic, and takes place with incandescence below 500°. Lithium behaves in an identical manner. Toward 650° magnesium decomposes fluoride of glucinum, under the same conditions. At the same temperature aluminium melts in contact with this compound without any reaction taking place.

To sum up, we have shown that the method of preparation given by Berzelius for obtaining a fluoride of glucinum leads to the formation of an oxyfluoride of practically constant composition, corresponding to the formula $5GlF_2,2GlO$; and, further, we have succeeded in preparing the anhydrous fluoride GlF_2, and have studied its principal properties.—*Comptes Rendus*, vol. cxxvi., No. 20.

ON A BOROCARBIDE OF GLUCINUM.

By P. LEBEAU.

We have previously announced (*Comptes Rendus*, cxxiii., p. 818) that boron had the power of reducing glucina at the temperature of the electric furnace; we now propose to study the compounds of boron and glucinum which may possibly be formed in this reduction.

Pure glucina, procured by the calcination of nitrate of glucinum, was mixed with a quantity of boron sufficient to remove all the oxygen and produce a boride. The actual proportions used were;—

Pure glucina	75 parts
Boron	45 ,,

These were thoroughly mixed, moistened with alcohol and compressed into the form of little cylinders, which were then dried by being left for some hours in an oven at 150°. One of these little cylinders was placed in a carbon boat, in a tube of the same material, and heated in the electric furnace. The heating lasted for seven or eight minutes with a current of 950 ampères and 45 volts. At the termination of the experiment the mass was found to be in a state of tranquil fusion. After cooling, a homogeneous material with a metallic appearance and a crystalline fracture was found in the boat.

This experiment was repeated on a much larger quantity of material in a carbon crucible. A button was formed at the bottom of the crucible, very hard, and of which the greater portion was metallic-looking and well-crystallised. In some places a white substance having undergone fusion could be distinguished; this was un-

reduced glucina. The metallic particles, collected with great care, were found to contain free glucina, and qualitative analysis showed that they were composed of carbon, boron, and glucinum. This substance is without action on water, even after several days' contact; the carbon is therefore not in the form of a carbide of glucinum easily decomposable by water, but, on the contrary, enters into a triple combination of carbon, glucinum, and boron.

The analysis of this compound was carried out in the following manner:—

1. *Estimation of the Boron and the Glucinum.* — A known weight of the material was attacked by nitric acid in the apparatus used by M. Moissan for estimating boron by Gooch's method. The boric acid entangled by the methylic alcohol was obtained directly by the increase in weight of a known quantity of quicklime. The residue remaining in the flask in which the attack took place was taken up with water, and thrown on a tared filter to get the weight of unreduced glucina which is insoluble under these conditions. The filtered liquor was precipitated with ammonia, and a small quantity of sulphide of ammonium added. The precipitate was weighed after calcination.

2. *Estimation of the Carbon.*—The carbon was estimated in the form of carbonic acid, the material being attacked by chromic acid in sulphuric solution. The arrangement of the apparatus was practically identical with that described by M. Carnot for the estimation of the carbon in irons and steels.

By deducting the quantity of unreduced glucina we obtained the following proportions between the weights of the carbon, the boron, and the glucinum combined:—

Carbon	27·99	28·34
Boron	29·18	39·12
Glucinum ..	32·83	32·54
		99·99

These figures have led us to give the formula $C_4Bo_6Gl_6$, or $Bo_6C.3CGl_2$, to this carboboride of glucinum:—

	Calculated for $C_4Bo_6Gl_6$.
Carbon	28·49
Boron	39·17
Glucinum	32·33

Borocarbide of glucinum occurs in brilliant crystals with a metallic lustre, having a density of about 2·4. It does not change in air at the ordinary temperature; heated to redness it oxidises superficially.

In a current of pure oxygen at about 700° the presence of carbonic acid may be detected, but the reaction stops rapidly, the layer of boric acid formed protecting the rest of the substance from any deeper oxidation.

Towards 45° borocarbide of glucinum burns in chlorine with a beautiful incandescence, chloride of boron and chloride of glucinum being produced, while a black residue remains consisting of amorphous carbon. Bromine gives an identical result; iodine is without action up to the softening point of glass. By operating in porcelain we noticed a very distinct reaction, with the production of iodide of glucinum and iodide of boron. In the vapour of sulphur, at a red heat, the attack takes place superficially; the residue when moistened with water gives off sulphuretted hydrogen.

The gaseous hydracids also react on the borocarbide of glucinum. The mineral acids, and particularly nitric acid, dissolve it rapidly.

We have not been able, in the reduction of glucina by boron in the electric furnace, to obtain any compound free from carbon. The reduction takes place at a very high temperature, and it was impossible for us to protect the matter from the vapours of carbon.—*Comptes Rendus*, vol. cxxvi., No. 19.

ON THE ABSORPTION OF NITRIC OXIDE BY FERROUS SALTS.

By V. THOMAS.

In a preceding paper, I showed that all ferrous salts, in whatever solution, absorbed nitric oxide, but that this absorption was more or less great according to the solvent used. I will here show, by referring to numerous experiments, that this absorption is not proportional to the minimum weight of iron contained in the solution, but that *it is a function of the nature of the salt.*

Absorption of Binoxide of Nitrogen by Ferrous Bromide. Solvent used: Water.

The absorptions were determined by weight and by volume.

Absorption by Weight.—A certain weight of bromide was dissolved in a quantity of boiled water, variable according to experience. To the solution iron filings were added, which, by prolonged boiling, collected all traces of the per-salt which might have been formed during the solution. This solution should be made in a flat-bottomed flask. In this flask a tube reaching below the surface of the liquid serves to convey a current of inert gas (CO_2 or H for preference). Another tube serves for the escape; this tube should be drawn out before the blowpipe, and should enter the lateral tube of a bulb gas-washer. This washer should be carefully tared. It is filled with the ferrous solution, taking care to exclude all air. For this purpose the lower end of the tube leading the gas into the flat-bottomed flask was kept above the surface of the liquid, while the other end was plunged into the solution. After having completely driven the air out of the apparatus, the binoxide of nitrogen was slowly passed through. This was partially absorbed, while the excess, carrying with it a little watery vapour, was passed through U-tubes filled with pumice-stone soaked in sulphuric acid and previously tared.

We could thus easily deduce the quantity of gas absorbed.

The contents of the washer were then collected, and on a known portion of the solution the iron was estimated in the state of oxide; this easily gives the concentration of the liquor.

Experiments below 10°. *Temperature* 6°.

I. Weight of iron dissolved	0·3795
Concentration of the liquor.. ..	0·75 per cent
Absorption	0·1360
II. Weight of iron dissolved	0·4970
Concentration of the liquor.. ..	0·6 per cent
Absorption	0·1740

Experiments above 10°. *Temperature* 10—12°.

I. Weight of iron dissolved	1·4846
Concentration of the liquor.. ..	2·5 per cent
Absorption	0·4045
II. Weight of iron dissolved	0·6230
Concentration of the liquor.. ..	1·25 per cent
Absorption	0·1665

If we calculate the percentage of iron into NO we get—

	I.	II.
Below 10°	35·1	35 0
Above 10°	27·2	26·6

Absorption in Volumes.—The method of operating has been described in a preceding note. We here give the results of the experiments. (See Table A).

Table A.

I.	2	c.c. of a solution containing	5·978	grms.	Fe per 100 c.c. absorbed	30	c.c. NO at	6°
II.	9·1	,, ,,	5·978	,,	,, ,,	97	,,	10°
III.	2·8	,, ,,	5·978	,,	,, ,,	53	,,	−5°
IV.	2·8	,, ,,	5·978	,,	,, ,,	45	,,	6°
V.	3·5	,, ,,	5·978	,,	,, ,,	38·5	,,	11°
VI.	3·7	,, ,,	5·978	,,	,, ,,	47	,,	8°
VII.	2·3	,, ,,	5·978	,,	,, ,,	25	,,	8°
VIII.	4·1	,, ,,	5·978	,,	,, ,,	65	,,	2°
IX.	3·5	,, ,,	5·978	,,	,, ,,	38·9	,,	8°
X.	2·9	,, ,,	5·978	,,	,, ,,	29·9	,,	10°
XI.	3	,, ,,	5·978	,,	,, ,,	29·5	,,	10°
XII.	2	,, ,,	5·978	,,	,, ,,	36·5	,,	0°
XIII.	1·5	,, ,,	59·978	,,	,, ,,	25·4	,,	4°
XIV.	3·5	,, ,,	59·978	,,	,, ,,	22 7	,,	20·5°
XV.	3·5	,, ,,	59·978	,,	,, ,,	50·7	,,	4°
XVI.	2·5	,, ,,	59·978	,,	,, ,,	41	,,	7°

Table B.

I.	11·2	c.c. of a solution containing	0·789	grm.	Fe per 100 c.c. absorbed	21	c.c. NO at	17°
II.	16 5	,, ,,	0·789	,,	,, ,,	28	,,	18°
III.	11 3	,, ,,	0·789	,,	,, ,,	24·5	,,	13°
IV.	8	,, ,,	3·110	grms.	,, ,,	52	,,	16°
V.	4·8	,, ,,	3·110	,,	,, ,,	47	,,	12°
VI.	8	,, ,,	3·110	,,	,, ,,	54	,,	15°
VII.	5	,, ,,	3·110	,,	,, ,,	44	,,	14°

Table C.

I.	12·2	c.c. of a solution containing	3·171	grms.	Fe per 100 c.c. absorbed	58	c.c. NO at	16°
II.	9·6	,, ,,	3·171	,,	,, ,,	45	,,	13°
III.	8·5	,, ,,	2·926	,,	,, ,,	36	,,	−3°
IV.	5·8	,, ,,	2·926	,,	,, ,,	19	,,	18°
V.	8·3	,, ,,	2·926	,,	,, ,,	37	,,	13°

Table D.

I.	8	c.c. of a solution containing	1·925	grm.	Fe per 100 c.c. absorbed	23	c.c. NO at	15°
II.	9·1	,, ,,	1·925	,,	,, ,,	26	,,	21°
III.	9	,, ,,	1·925	,,	,, ,,	27	,,	12°

By examining the different proportions of NO present per cent of iron we get the following averages :—

Between	−5° and 0°	41·73 per cent
,,	0° ,, 7°	35·87 ,,
,,	8° ,, 11°	24·90 ,,
At	20·5°	15·43 ,,

From these numerous determinations we can deduce that ferrous bromide does not exactly follow M. Gay's law; especially as, while with ferrous chloride the proportion of binoxide of nitrogen is 34·78 per 100 of iron at 12°, it is necessary, in order to get a similar absorption with bromide, to work at a temperature between 0° and 7°; and while towards 20° the chloride absorbs a quantity of gas corresponding to 26 per cent of the weight of iron, the bromide absorbs only 15 per cent of binoxide of nitrogen. When using an alcoholic solution, the results obtained are quite comparable.

Solvent used: Absolute Alcohol.—The absorptions were determined by volume (see Table B). The figures represent the following proportions of NO present :—

I.	At 17°	28·33
II.	,, 18°	25·59
III.	,, 13°	35·52
IV.	,, 16°	28·02
V.	,, 12°	42·24
VI.	,, 15°	29·06
VII.	,, 14°	37·94

The same experiments made with the chloride at about 17° give a figure higher than 50 per cent of gas (per cent of iron). We must therefore conclude that the absorption is less with the bromide than with the chloride. Experiments made with the iodide lead to entirely analogous results.

Absorption of Binoxide of Nitrogen by Ferrous Iodide.

Solvent used: Water.—The absorptions were determined by volume (see Table C). The proportions of nitric oxide present per cent of iron are :—

I.	At 16°	18·29
II.	,, 13°	19·28
III.	,, −3°	20·62
IV.	,, 18°	17·41
V.	,, 13°	20·43

It is as well to remark here that temperature has but little influence on gaseous absorption.

Solvent used: Alcohol.—(See Table D). The proportions of NO present in percentages of iron are :—

I.	At 15°	20·00
II.	,, 21°	19·95
III.	,, 12°	20·89

The same remark again applies here. In a future paper I propose developing some conclusions resulting from these experiments.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 8.

A DETERMINATION OF THE ATOMIC WEIGHT OF PRASEODYMIUM AND OF NEODYMIUM.*

By HARRY C. JONES.

(Concluded from p. 282).

THE method first employed consisted in dissolving the superoxide in sulphuric acid, evaporating the solution of the sulphate to dryness, and heating it in a platinum vessel to a temperature above the boiling-point of sulphuric acid. The sulphate was then weighed, dissolved in water to form a very dilute solution, strongly acidified with hydrochloric acid, and the sulphuric acid precipitated by means of barium chloride. It was hoped that by using a very dilute solution, strongly acidified, it would be possible to precipitate all of the sulphuric acid as the barium salt. Several determinations were made, but the results obtained were so discordant as to be entirely valueless. The presence of praseodymium was shown in the precipitate, even after it had been boiled with excess of barium chloride for a considerable time. This fact had been pointed out by Marignac (*loc. cit.*), but it was hoped that by working in very dilute solutions, which had been strongly acidified, the difficulty could be overcome. It could not, and the method had to be abandoned as entirely useless for the purpose of an atomic weight determination.

The method adopted consisted in reducing the superoxide to the sesquioxide in an atmosphere of hydrogen, and converting the sesquioxide into the sulphate. The details of the process are as follows :—

A weighed amount of the superoxide was placed in a porcelain boat, and this within a hard-glass tube, which rested upon a combustion furnace. A stream of hydrogen gas, which had been washed in a solution of sodium plumbate, to remove hydrogen sulphide, and in silver nitrate to remove arsine, was dried over calcium chloride, and passed through the tube. The superoxide was easily reduced to the sesquioxide on heating. The sesquioxide was allowed to become perfectly cold in the current of hydrogen, and boat and contents were then removed from the tube and weighed. The boat containing the sesquioxide was then returned to the glass tube and re-heated in an atmosphere of hydrogen. In no case was there any change in weight caused by the second heating.

A platinum crucible was placed within a ground-glass stoppered weighing-tube, which was then closed and weighed. The sesquioxide was poured from the boat into the crucible, and the whole was re-weighed. This gave the weight of the sesquioxide used in a determination.

A considerable excess of sulphuric acid, of medium concentration, was added to the crucible. An equal volume of the sulphuric acid used was placed in a weighed platinum crucible, evaporated to dryness, and heated exactly as in carrying out a determination, to see whether there was any appreciable residue left behind. In no case did the weight of the crucible increase more than 0·00005 grm., which was therefore negligible. The platinum crucible, containing the oxide and sulphuric acid, was placed in an air-bath constructed of thick sheet copper, and closed at the bottom by a piece of very thick sheet copper. The sides of the bath were thickly covered with asbestos paper. The platinum crucible rested upon a porcelain triangle, about an inch from the bottom of the air-bath. Heat was applied to the bath, very gently at first, to avoid all spattering, and then increased, until the solution of the sulphate had evaporated nearly to dryness. Then the bath was heated more strongly, and finally raised to a temperature above the boiling-point of sulphuric acid. The sulphate was maintained at this temperature for some hours, and then weighed. It was re-heated and re-weighed, and this continued until constant weight was reached. To determine whether only the normal sulphate was present, purified ammonium carbonate was added, and the crucible and contents again heated above the boiling-point of sulphuric acid. There was no change in the weight of the sulphate, showing that only the normal sulphate of praseodymium was present. The sulphate thus prepared was perfectly soluble in water. I was completely unable to verify the observation of Bailey (*J. Chem. Soc.*, li., 676), who stated that "the sulphate was made into a paste with sulphuric acid and heated at 360°. . . . . An approach to a constant weight was manifest, but variations amounting to a m.grm. or more occurred, and with each successive increase of temperature the loss was accelerated. No range of temperature could be found within which the salt remained perfectly constant."

I found that the weight of the sulphate remained perfectly constant through a considerable range of temperature, provided the temperature to which it had been heated was sufficient to remove all the excess of sulphuric acid and decompose any acid sulphate. It is possible that Bailey did not heat the sulphate, or in his case the mixture of praseodymium and neodymium sulphates, to a temperature sufficiently high to leave only the normal sulphate. This is the only way I can account for the result which he obtained.

The crucible containing the sulphate was removed from the air-bath as quickly as possible and placed in the weighing-tube. This was closed and placed in a desiccator over phosphorus pentoxide and allowed to cool. The sulphate was then weighed in the closed tube, which is necessary, since it absorbs moisture rapidly from the air.

The Results.

	Pr_2O_3.	$Pr_2(SO_4)_3$.	$3(SO_3)$.	{O=16 S=32·07} At. wt. Pr.	{O=15·88 S=31·83} At. wt. Pr.
1	0·5250	0·9085	0·3835	140·42	139·37
2	0·6436	1·1135	0·4699	140·50	139·45
3	0·7967	1·3788	0·5821	140·38	139·33
4	0·7522	1·3018	0·5496	140·38	139·33
5	0·7788	1·3473	0·5685	140·53	139·48
6	0·6458	1·1172	0·4714	140·54	139·49
7	0·6972	1·2062	0·5090	140·51	139·46
8	0·7204	1·2464	0·5260	140·49	139·44
9	0·8665	1·4990	0·6325	140·54	139·49
10	0·6717	1·1624	0·4907	140·40	139·35
11	0·7439	1·2873	0·5434	140·42	139·37
12	0·6487	1·1224	0·4737	140·47	139·42
	8·4905	14·6908	6·2003	140·46	139·41

The average of the individual determinations is 140·46 when oxygen = 16, or 139·41 when oxygen = 15·88. The difference between the highest and lowest value is 0·16. This series represents all of the determinations which were made, with the exception of two, which were lost by accident and never completed.

The atomic weight of praseodymium, as calculated from the total oxide used, and total sulphate formed, is 140·47 when O=16, or 139·41 when O=15·88.

The sesquioxide, prepared by reducing the superoxide in a current of hydrogen, always liberates a small amount of gas when dissolved in sulphuric acid. This is probably occluded hydrogen. The amount of gas thus set free was determined approximately, and found to be so small that it could be disregarded.

The atomic weight of praseodymium, as here determined, may be taken as 140·45 when oxygen = 16, or 139·4 when oxygen = 15·88. This result lays no claim to very great accuracy, because of the apparent impossibility of obtaining an absolutely pure praseodymium compound. However, considering the result of the careful spectroscopic analysis which was made of the material

* From the *American Chemical Journal*, vol. xx., No. 5.

which I employed, and all the errors which could possibly have entered into the determinations, I see no reason to think that the result can differ from the true atomic weight of praseodymium by more than 0·2 of a unit.

The Atomic Weight of Neodymium.

Somewhat more than 2 kilogrms. of the double nitrate of neodymium and ammonium were furnished me by Mr. Shapleigh. This was analysed spectroscopically, and found to contain praseodymium and also a trace of lanthanum. The substance was further purified by fractional crystallisation, as described for praseodymium. The entire material was dissolved in water, to which a little nitric acid had been added and evaporated, until, on cooling, about 1/15 to 1/20 crystallised out. A considerable volume of nitric acid was then added, and the larger part of the double salt allowed to separate on further concentrating the solution. The mother-liquor was then carefully filtered from the crystals. The first and third fractions were discarded, and the second preserved for further treatment. The middle fraction was then treated exactly as the original substance had been, was separated into three fractions, and the middle one preserved and again treated in the same manner. This process was repeated twenty-seven times.

The middle fraction of the last crystallisation was dissolved in water, strongly acidified with nitric acid, and poured into a dilute solution of oxalic acid, in the same manner as described under praseodymium. This would separate such common impurities as iron, calcium, &c. The oxalate was washed with great thoroughness, dried, and decomposed in a platinum crucible over the blast-lamp. The oxide of neodymium, thus prepared, was again analysed spectroscopically. It was found to contain praseodymium and a trace of lanthanum. The same method was employed to separate the trace of lanthanum as in the case of the praseodymium salt.

The praseodymium which remained in the double salt of neodymium could not be separated by any known method, and must therefore be determined. The amount present was ascertained with considerable accuracy by studying the intensity of the absorption bands, and comparing these with the absorption bands of the pure praseodymium salt of known concentration. The exact method is that described under praseodymium. It was found that the double nitrate of neodymium and ammonium contained 1·6 per cent of the double nitrate of praseodymium and ammonium.

After the lanthanum was separated the neodymium was again precipitated as the oxalate, with oxalic acid, in the presence of nitric acid, by the method already described. The oxalate was converted into the oxide by heating in a platinum crucible over the blast-lamp. The oxide thus obtained was analysed spectroscopically, special attention being given to the presence of thorium. The only impurity which could be detected was praseodymium, the amount of which had already been determined.

The oxide of neodymium, obtained from the oxalate, does not possess any property of a superoxide as such. It dissolves in sulphuric acid without the evolution of oxygen. When heated in a current of hydrogen exactly as the oxide of praseodymium obtained from the oxalate, it does not change in weight. When hot, the oxide has a marked bluish colour, which, however, disappears on cooling. It will thus be seen that the substance which I employed in determining the atomic weight of neodymium had all the properties described by Von Welsbach (*Monatsh. Chem.*, vi., 489), as characteristic of the sesquioxide of neodymium.

The method employed in determining the atomic weight of neodymium was the same, in general, as that used in the case of praseodymium. After it had been found that the oxide obtained from the oxalate did not change in weight when heated in a current of hydrogen, this part of the process was abandoned. The oxide was, however, heated in the platinum crucible just before weighing, and allowed to cool in a desiccator over phosphorus pentoxide, to remove every trace of moisture. The method of synthesising the sulphate from the oxide, and heating and weighing the sulphate, was the same as employed with praseodymium.

The Results.

	Nd_2O_3.	$Nd_2(SO_4)_3$.	$3SO_3$.	{O=16, S=32·07} At. wt. Nd.	{O=15·88, S=31·83} At. wt. Nd.
1	0·8910	1·5296	0·6386	143·58	142·50
2	0·7880	1·3530	0·5650	143·51	142·43
3	0·9034	1·5509	0·6475	143·57	142·49
4	0·7668	1·3166	0·5498	143·51	142·43
5	0·8908	1·5296	0·6388	143·49	142·41
6	0·8848	1·5194	0·6346	143·46	142·38
7	0·8681	1·4903	0·6222	143·57	142·49
8	0·8216	1·4103	0·5887	143·62	142·54
9	0·8531	1·4646	0·6115	143·56	142·48
10	0·8711	1·4957	0·6246	143·50	142·43
11	0·8932	1·5332	0·6400	143·62	142·54
12	0·8893	1·5268	0·6375	143·55	142·47
	10·3212	17·7200	7·3988	143·55	142·47

The average of the twelve determinations is 143·55 when oxygen = 16, or 142·47 when oxygen = 15·88. The difference between the highest and lowest value is 0·16. Three determinations were lost by accident. The atomic weight of neodymium, calculated from the total amount of oxide used and sulphate formed, is 143·55 when oxygen = 16, or 142·47 when oxygen = 15·88.

The value of the atomic weight of neodymium thus found must be corrected for the presence of praseodymium, which has an atomic weight about three units lower. The final value, which, from my work, I should assign to the atomic weight of neodymium, is 143·6 when oxygen = 16, or 142·52 when oxygen = 15·88. I think this value can be regarded as accurate to within about the same limits as indicated in the case of praseodymium.

The oxide of neodymium, prepared as above described, liberated a small amount of gas, presumably air, when dissolved in sulphuric acid. But since this work lays no claim to the last degree of accuracy, due chiefly to the impossibility of effecting complete separations of the rare elements, such corrections were found to be less than the necessary experimental error.

The values which I obtained for the atomic weights of praseodymium and of neodymium differ widely from those given by Von Welsbach (*Monatsh. Chem.*, vi., 490). It is impossible to determine from the paper of Von Welsbach what he regarded as the atomic weight of oxygen; but since no statement is made, the presumption is in favour of 16. The following comparison will show how widely the two results differ:—

	Von Welsbach.	My results.
Pr	143·6	140·45
Nd	140·8	143·6

There is a discrepancy of about three units in the case of each element. Indeed, if my values were reversed for the two elements, they would not differ widely from those of Von Welsbach.

It is not possible to account satisfactorily for the difference between my results and those of Von Welsbach, since the latter has given no details pertaining to his determinations. The fact that if either set of results were interchanged for the two elements they would agree with the other, suggests that possibly the discrepancy arose in a typographical error in the paper of Von Welsbach, in which his values are recorded as tentative, and in less than a line.

THE ACTION OF CARBON DIOXIDE ON SOLUBLE BORATES.*

By LOUIS CLEVELAND JONES.

In a process for the separation and estimation of boric acid devised by Morse and Burton (*Am. Chem. Journ.*, x., 154), the liberation of carbonic, silicic, and boric acids from a mixture of inorganic salts is effected by the action of sulphuric acid, using tropæolin OO as an indicator of acidity. In the solution thus prepared, containing in free condition only carbonic, silicic, and boric acids, the silicic acid is dehydrated and made insoluble by anhydrous copper sulphate. The boric acid is then extracted with absolute alcohol. To this alcoholic solution of boric acid a known amount of barium hydroxide solution is added in excess over that required to form a barium metaborate, BaB_2O_4. Carbon dioxide is then passed into the solution in accordance with the hypothesis that the excess only of barium is acted upon. The aqueous mixture of barium metaborate and barium carbonate is evaporated, and the residue is heated to a constant weight over a triple burner. From the following proportion the boric acid present may be calculated:—

> The molecular weight of boric acid – the molecular weight of carbon dioxide : the molecular weight of boric acid = the total weight found – the theoretical weight of barium as carbonate : the weight of boric acid present.

It is obvious, inasmuch as the difference between the calculated weight of the barium as carbonate and the actual weight of the residue is multiplied nearly three times to get the boric oxide, that the actual error of the process, whatever it may be, is magnified three-fold by the method of computation.

I have made a study of this method applied to pure boric acid, but have been unable to obtain results similar to those of Morse and Burton.

For this investigation boric acid of standard strength was made by dissolving in a given amount of water a known weight of anhydrous boric oxide, prepared by igniting over a blast lamp boric acid several times recrystallised and washed. A solution of barium hydroxide was filtered free from carbonate and then standardised by precipitation as carbonate and also by the Phelps method with iodine (*Am. Chem. Journ.*, ii., 70). To a measured amount of the boric acid solution an excess of barium hydroxide was added, carbon dioxide passed, and the whole evaporated and by successive ignitions brought to a constant weight. Below are tabulated some of the results (see Table, next column).

Plainly the results vary with the degree of the ignition. At the outset the residue may or may not weigh more than the theory requires for the known amounts of barium hydroxide and boric acid taken upon the assumption that the residue is barium metaborate and barium carbonate. This is obviously natural, if the carbon dioxide acts upon the barium borate as well as upon the excess of barium hydroxide; for, it is to be expected that in the evaporation more or less of the free boric acid will volatilise, and that in the subsequent ignition the boric acid remaining will tend to re-combine more or less completely, replacing carbon dioxide. If the boric acid present were to re-combine completely with the barium carbonate to form a metaborate, the final result would always be low by just the amount of free boric acid volatilised in the process of evaporation and ignition. The evidence of an experiment, however, in which 0·25 grm. of previously prepared barium metaborate was fused in contact with 0·5 grm. of barium carbonate, resulting in a loss of 0·0871 grm., goes to show that the metaborate and carbonate of barium interact still further to liberate carbon dioxide.

	$Ba(OH)_2$ taken. Calculated as $BaCO_3$.	B_2O_3 taken.	Weight of residue after successive ignitions.	B_2O_3 found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.
I.	0·9391	0·2200	1st wt., 0·9860	0·1263	−0·0937
			2nd ,, 0·9786	0·1063	−0·1137
II.	0·9318	0·1295	1st ,, 0·9605	0·0744	−0·0523
			2nd ,, 0·9558	0·0646	−0·0649
			3rd ,, 0·9510	0·0517	−0·0778
III.	0·9253	0·2192	1st ,, 1·0357	0·2972	+0·0780
			2nd ,, 1·0248	0·2679	+0·0487
			3rd ,, 1·0149	0·2412	+0·0220
			4th ,, 1·0064	0·2183	−0·0009
			5th ,, 0·9975	0·1944	−0·0248
			6th ,, 0·9855	0·1621	−0·0671
IV.	0·7301	0·0810	1st ,, 0 8017	0·1927	+0·1117
			2nd ,, 0·7777	0·1281	+0·0471
			3rd ,, 0·7642	0·0918	+0·0108
			4th ,, 0·7582	0·0757	−0·0053
			5th ,, 0·7517	0·0582	−0·0228
			6th ,, 0·7482	0·0487	−0·0323
			7th ,, 0·7447	0·0393	−0·0417
			8th ,, 0 7427	0·0339	−0·0471
			9th ,, 0·7422	0·0326	−0·0484
			10th ,, 0·7407	0·0285	−0·0525

These results were so surprising in the light of the experience of Morse and Burton that the question of the possibility of breaking up by carbon dioxide the barium metaborate already formed was put to the test directly. A known amount of barium hydroxide was taken in solution and to it added an amount of boric acid very little in excess of that theoretically necessary to form the barium metaborate. The solution was evaporated to dryness and the residue ignited. The weight obtained proved to be 0·0008 grm. less than the sum of the barium and boric oxides taken, doubtless because the slight excess of boric acid was somewhat volatile in the evaporation. The mass, presumably barium metaborate, was now dissolved as completely as possible in hot water, carbon dioxide was passed through the solution, the whole was evaporated, and the residue ignited and weighed. The increase in the weight showed that carbon dioxide had been absorbed, while a corresponding amount of boric acid had not volatilised.

	$Ba(OH)_2$ taken. Calculated as $BaCO_3$.	B_2O_3 taken.	Residue after ignition.	Residue after CO_2 treatment and ignition.
	Grm.	Grm.	Grm.	Grm.
V.	0·8377	0·2990	0·9491	−0·9771

After passing in carbon dioxide and igniting, the increase in weight was 0·0280 grm., representing the gas absorbed less the boric acid volatilised.

It was plain that barium metaborate is decomposed in solution by carbon dioxide. The possibility remained, however, that the action of carbon dioxide might be so regulated as to leave the metaborate practically unattacked. In experiment VI., therefore, carbon dioxide was passed above the stirred solution until no further precipitate formed upon the surface, the barium present being in excess of that required to form a metaborate.

	$Ba(OH)_2$ taken. Calculated as $BaCO_3$.	B_2O_3 taken.	Weight of residue after ignition.	B_2O_3 found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.
VI.	0·7094	0·2070	0·7710	0·1658	−0·0412

The variation of this result from the theory shows that under these conditions the metaborate is not unaffected by carbon dioxide, the loss being due, of course, to the escape of boric acid.

An attempt was now made therefore to gauge the amount of the carbon dioxide introduced by means of an indicator. In Experiment VI. phenolphthalein was added to the solution of boric acid containing an excess

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. v., p. 442.

of barium hydroxide, and the current of gas was stopped when the colour of the indicator disappeared.

	$Ba(OH)_2$ taken. Calculated as $BaCO_3$.	B_2O_3 taken.	Weight of residue after ignition.	B_2O_3 found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.
VII.	0·6073	0·1573	1st wt., 0·6820	0·2011	+0·0438
			2nd ,, 0·6783	0·1911	+0·0338
			3rd ,, 0·6720	0·1742	+0·0169
			4th ,, 0·6700	0·1688	+0·0115
			5th ,, 0·6655	0·1567	−0·0006
			6th ,, 0·6630	0·1499	−0·0074
			7th ,, 0·6609	0·1443	−0·0130

This result is manifestly an improvement over those obtained without the careful restriction of the supply of carbon dioxide. A similar experiment, differing only in the single point that the carbon dioxide was made to act upon a boiling solution, resulted in like manner.

In the light of these observations it is plain that a sufficiently prolonged action of carbon dioxide should result in the displacement of all the boric acid if that acid can be removed from the field of action as fast as it is liberated. Experiments were made which clearly demonstrate the truth of this hypothesis. A small side-necked flask was charged with a solution of boric acid (0·1143 grm.) and barium hydroxide (0·3227 grm.) in proportion to form the metaborate. The mass was brought nearly to dryness by distillation and methyl alcohol (15 c.m.³) added. Through this flask, in which the alcohol was kept boiling by a Bunsen burner, was passed the vapour of methyl alcohol, while carbon dioxide, purified by a neutral solution of silver nitrate, bubbled continually through the entire system. The methyl alcohol vapour coming from the side-neck flask was kept lighted by contact with the flame of a Bunsen burner and the distillation continued for two hours—until the flame showed not the slightest tinge of green. The residue in the flask originally containing barium metaborate was brought to dryness and tested for boric acid. Only a trace was found, and this was thought to be due to inclusion by the insoluble barium carbonate. In a similar experiment, in which borax was used instead of barium borate, no trace of boric acid was found in the residue of sodium carbonate, either by turmeric or the flame test, while the distillation was continued only one-half the time of the preceding experiment. This result is quite in harmony with the views of P. Georgevic (*Journ. Prakt. Chim.*, xxxviii., 118) to the effect that the large absorption of carbon dioxide in solutions of borax indicates that the boric acid is displaced from its union with the base.

Obviously, the division of the base between boric acid and carbonic acid falls under the principle of mass action, and if the boric acid is taken in sufficient excess over the barium hydroxide, the action of the carbonic acid should be inappreciable. This idea is sustained by an experiment in which about 1 grm. of boric acid was dissolved with 0·15 grm. of barium hydroxide. No precipitate could be obtained by passing carbon dioxide and boiling. In fact, in the French process of borax manufacture just this action of an excess of boric acid upon a boiling solution of sodium carbonate is used. On the other hand, to prevent the formation of a carbonate this excess of boric acid must be considerable if the action of carbon dioxide is prolonged. Thus, in an experiment in which a current of carbon dioxide was passed into a solution containing 0·1219 grm. of boric anhydride and one-half the amount of barium needed to form a metaborate, the solution (60 c.m.) deposited on boiling 90 per cent of the barium present in the form of the carbonate.

In view of the facts which I have described, it is difficult to see under what conditions Morse and Burton prevented the excessive action of carbon dioxide and obtained in their analytical method the excellent results which they record.

I wish to express my thanks to Professor Gooch, whose advice has been constantly sought and freely given.

NEW CONSTITUENTS OF THE ATMOSPHERE.

At the meeting of the Royal Society on June 9th, Professor Ramsay and Mr. Morris Travers described their identification of a new constituent in atmospheric air, which they designated krypton. At the same time they intimated that, quite recently, during their investigations, they had found indications of another gas which afforded every promise of being also a novelty. They have now completed a preliminary examination of this constituent, and gave an outline of its nature and history at the meeting of the Royal Society on June 16th.

The discovery has been made in the course of a series of researches into the nature of argon which has occupied them for many months at the laboratory in University College, and in which they have been greatly aided by having at their disposal the apparatus devised by Dr. Hampson for liquefying air in large quantities. In view of these researches, they had provided themselves with a large quantity of the gas argon, the discovery of which in atmospheric air was announced by Lord Rayleigh and Professor Ramsay in 1895—altogether, some 18 litres, or, in other words, about 15 quarts. Already the latter investigator, in conjunction with Dr. Norman Collie, had attempted to separate the argon—in which they already suspected the presence of a second constituent in small quantities—into a lighter and heavier section, by diffusion, but, though they met with partial success, the difference in density between the two parts was so slight that they hesitated to draw the conclusion that the argon with which they were dealing was in reality a composite substance. But the experiments with helium which, as described at the Toronto Meeting of the British Association, were carried on by Messrs. Ramsay and Travers, in hope of finding a new gas intermediate between it and argon, led them to the conclusion that the greatest difficulty attended the attempt to separate a very small portion of a heavy gas from a large quantity of a light one by the means of diffusion; so they determined, since they had the use of Dr. Hampson's apparatus, to attack the problem in quite another way.

A quantity of argon was liquefied. It formed a colourless fluid, but at the same time a considerable quantity of a solid substance was observed to separate, partially round the sides of the tube and partially below the surface of the liquid. But this more conspicuous material was not all. A gas also remained, which was at once removed for further examination. After that they turned their attention to the frozen material, which was also separated by processes which they described. The light gas, which was the immediate subject of their investigation, was first examined. The spectrum was characterised by a number of bright red lines, one being particularly brilliant, and a yellow one of similar intensity. Green and blue lines were numerous, but inconspicuous. The yellow line is as intense as those in sodium, helium, and krypton, but is not identical with them. Next, an effort was made to ascertain the density of the gas. The results of their experiment led the investigators to the conclusion that they had not as yet obtained it in a perfectly pure condition. A sample, taken off at an early stage, gave a density of 17·2; at a later one, however, it was reduced to 14·67. But this is still too high if the new gas conforms to the Periodic Law—for, in that case, it should not exceed 11. It may, however, be lowered by further purification. But these tests, and sundry others, suggest that, even if not yet obtained in an absolutely pure condition, this gas is a new element, for which, accordingly, the name *Neon* is proposed. They next turned their attention to the solid—the material frozen out of argon. Its spectrum proved to be very complex, but totally different from that of argon, and its behaviour at low temperatures was markedly different, though its density was practically identical. It was proved to consist of a single element. This substance, accordingly, which was separated by freezing out of argon,

must be a distinct elementary body, though in some respects in close relationship with it, so they propose to name it *Metargon*. In fact, as the investigators observe, it occupies the same position in regard to argon that nickel does to cobalt, having the same atomic weight, yet different properties.

In this account no mention is made of krypton, the discovery of which was announced last week. Naturally it will be asked why the investigators did not again come across it. They attribute its absence to one, or possibly both, of two causes. In order to prepare it they would have required a sample not less than sixty thousand times the volume of that which they used in the above-mentioned experiments, and, besides this, metargon is a solid at the temperature of boiling air, while krypton is probably volatile. Moreover, the air from which they originally obtained the latter gas had been filtered, and thus separated from metargon. Spectroscopic investigation, which has been undertaken by Mr. Baly, will have to be carried further, and, if possible, applied to more highly purified samples, before these new elements can be completely known. The results of such investigation may account, as was intimated in the course of the discussion, for certain peculiarities in the spectrum of argon which, when this gas was first separated, led more than one experienced investigator to doubt whether it was in reality a single element, and not a compound of at least two. This question will be settled by a careful comparison of the spectra of argon and metargon, when it will be ascertained whether the lines in the former, which had caused doubt, disappear when a perfectly pure sample of it is examined, but are found to occur in the spectrum of metargon. Messrs. Ramsay and Travers expressed themselves fully sensible of the importance of following up these hints, and stated that they had prepared a quantity of thoroughly pure argon, which they trusted would be before long subjected to spectroscopic examination, while the spectra of krypton and neon would be watched at every stage as they were obtained, and especially the latter, in a more and more pure condition. One of the greatest difficulties in such investigations is the chemical inertness of these new gases. Still, the resources of chemical ingenuity are not exhausted.

The most interesting point which, in the case of neon, awaits further examination, is the determination of its density and atomic weight. As we have already said, a gas with a density of 10, or, at any rate, not more than 11, should exist, if the Periodic Law of Mendeleeff hold good, in the interval between argon and helium. It was this gas for which Professor Ramsay was hunting during the earlier part of last year. It was this which, as he described to the Chemical Section of the British Association at Toronto, he failed to obtain by methods of diffusion, though his experiments were numerous and varied. But this gas neon seems very likely to be the missing link; its density has already been reduced by processes of purification from 17 to 14 (in round numbers), and the investigators are convinced that a further lowering will be made as they continue their experiments. It is then highly probable, we might venture to say almost certain, that neon will ultimately prove to be the gas which managed to elude them on the first search. The moral is the homely one, "Try again" but by some other way.

Not the least suggestive part of the remarkable discoveries which have signalised the closing month of the Royal Society's Session is the way in which one discovery has led on to another, and that which at first seemed only a feat of the laboratory has turned out to be an agent of research of the highest scientific value. When Pictet and Cailletet, rather more than twenty years ago, first liquefied air, they had probably little idea that they had done more than ascertain a fact of great scientific interest. But they had in reality laid the foundation-stone of a great superstructure of most important research. This idea was followed up by other investigators in various countries of Europe, including our own; their apparatus was improved, or new was devised, and now liquid air can be produced in large quantities, and at a comparatively moderate price. The researches of Professor Dewar at the Royal Institution, of Dr. Hampson in his own laboratory, and of Professor Ramsay, with Dr. Collie and Mr. Travers, have been to a very great extent dependent on this liquid. It might be said to have swept away a barrier during the last very few years, and to have revealed a widening field of scientific knowledge. Not only air, but such liquid gases as oxygen, nitrogen, and argon will all prove helpful in further investigations, and it would be idle to attempt to predict the results which may follow from their employment. Certain it is that the interesting researches which have been described this month are not likely to be the last, for the laboratories in Albemarle Street and Gower Street will be sure to vie one with another in striving to find out some new thing in the air we breathe, the water of springs, and the minerals of the earth.—*The Standard*, June 17th, 1898.

NOTICES OF BOOKS.

Laboratory Experiments on the Class Reactions, and Identification of Organic Substances. By A. A. Noyes, Ph.D., and S. P. Mulliken, Ph.D. Second Edition, thoroughly Revised. Pp. 28. Easton, Pa.: Chemical Publishing Company. 1897.

The primary object of the experiments herein described is to illustrate the characteristic reactions of organic substances, though the identification of unknown compounds is also a matter of great importance, and it is hoped by the authors that the student who intelligently follows the course of instruction here given will be able to devise methods for the detection and separation of other bodies not given in this volume.

The book is divided into three parts:—Part. I. gives experiments illustrating the class reactions of organic compounds, such as distinguishing double- and triple-bonded from single-bonded compounds; distinguishing hydrocarbons of different series; halogen compounds of different types; saturated and aromatic hydrocarbons, and their halogen derivatives from other compounds; various reactions, &c.

Part II. illustrates the methods of detecting nitrogen, sulphur, and halogens in organic compounds; and Part III. deals with the identification and separation of unknown organic substances.

We have thus a very useful and clearly written book, which will be of great service to the student working on organic chemistry.

French Self-taught, with Phonetic Pronunciation. By C. A. Thimm, F.R.G.S. London: E. Marlborough and Co. Pp. 93.

Although there is a great deal that is useful in this phrase book, we cannot admit that the author's phonetic method of teaching French pronunciation is altogether satisfactory—there is a great deal too much "g" in it; many of the words, though curious-looking (in some cases almost grotesque), must be admitted to be correct; but we do object to "soovaung" for "souvent," "maingtenaung" for "maintenant," "sepaundaung" for "cependant," &c. This is merely accentuating and encouraging what may be considered to be one of the chief faults in an ordinary Englishman's pronunciation of French, and one which shows imperfect teaching.

The general arrangement of the book and the choice of phrases and sentences are all that can be desired, and to anyone touring in France, with only a slight knowledge of the language, it will no doubt be of service.

Tables for Qualitative Chemical Analysis. ("Tafeln zur Qualitativen Chemischen Analyse"). By W. Hampe. Fourth Edition, Revised and Enlarged. Clausthal. 1897.

This collection of Tables for Qualitative Analysis, of which there are twenty-one in all, may be divided under three heads:—Tables I. to IX. are on the principal reactions of bases and acids; Tables X. and XI. on the testing of substances in the dry way; and Tables XII. to XXI. on the systematic method of procedure in qualitative analysis.

Though not arranged in the groups we are most familiar with in England, these tables will be of great use to the student who understands German. It is always well to know of more than one method of arriving at a wished-for result.

CORRESPONDENCE.

THE NEW GAS.

To the Editor of the Chemical News.

Sir,—Your anonymous correspondent of last week has omitted to mention the name of Lord Rayleigh, in attributing to me the announcement that argon is the inert constituent of atmospheric air; and also the name of Mr. Morris Travers, in connection with his remarks on Krypton. I hasten to correct these errors, which, doubtless through inadvertence, have escaped your notice.—I am, &c.,

William Ramsay.

University College, London,
Gower Street, W.C., June 21, 1898.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—Your correspondent, "Suum Cuique," apparently cannot see that Prof. Ramsay had added anything "to what Cavendish proved."

If I have formed a correct conception of Cavendish's work, he proved that if air contained any other substance than oxygen, nitrogen, and carbon dioxide, it did not exceed a certain small amount; though he actually isolated other gases, he never knew for certain that he had done so, and his account of his experiments was in such terms as to lead others of his day to believe that air was composed of only oxygen, nitrogen, and carbon dioxide. In fact Cavendish, as an experimenter, was in advance of his time, and his marvellous work was not capable of being properly interpreted till much later.

The history of the discovery of argon, &c., seems to me to have been thus:—The real discoverer was Lord Rayleigh, who observed that the density of atmospheric nitrogen was greater than that of chemical nitrogen: as a physicist, he doubtless felt that it would be desirable to associate himself with a chemist, and therefore Rayleigh and Ramsay isolated the constituent of air, which Cavendish did not know that he had obtained. So far, to my mind, the credit has been chiefly Lord Rayleigh's.

I am not aware that it was ever claimed that argon was proved to be an entity, and I gathered that Rayleigh and Ramsay had the possible mixed nature of argon constantly before their minds.

Next, led by the research of Hildebrand, Ramsay accidentally discovered helium; from this time I have gathered, from Ramsay's work, the possible mixed nature of both helium and argon was strongly before him. He spent many months trying to split up helium, and succeeded in separating a little argon, &c., from it: now it seems that he is attacking argon in the same way, and has already separated a gas which withstands the action of red-hot magnesium and calcium on one hand, and, on the other, sparking with oxygen in the presence of caustic soda; which is monatomic, which has a density greater than that assigned to argon, and which has a spectrum containing lines not belonging to any other body. On the whole of this evidence he concludes that there is a hitherto undescribed constituentof the atmosphere.

That Prof. Ramsay is fully alive to the possibility of other gases being present in the atmosphere, is shown by the fact that he and Mr. Travers have spent many months in the preparation for a search for another constituent. It is indeed chiefly in the careful work with the object of establishing the simple or mixed nature of helium, argon, &c., that the credit of Ramsay lies.

If it had not been for Rayleigh and Ramsay "Suum Cuique" would have probably lived in blissful ignorance of the classical experiment of Cavendish. As chemists have waited a century to learn "what Cavendish proved," cannot "Suum Cuique" wait a year or so, and give Prof. Ramsay time to do the work he has mapped out?—I am, &c.,

H. Droop Richmond.

Rodbourne, Claremont Road,
St. Margaret's, June 18, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société de Pharmacie de Bordeaux, January, 1898.

Glycerophosphates of Quinine. — E. Falières. — Glycerophosphate of quinine has been assigned the following formula, $C_3H_7O_3PO_3(C_{20}H_{24}N_2O_2)_2$, and described as small colourless crystals, in the form of needles, easily and completely soluble in warm water and in alcohol; it contains 68 per cent of quinine. It should be noticed that this formula applies to an anhydrous salt. The author's experiments show that the crystallised salt contains from 7 to 10 molecules of water, according to the degree of saturation of the acid by one or two molecules of quinine. Theory foresees and experiment confirms the existence of two glycerophosphates of quinine, corresponding to the sulphates or hydrochlorates known (the basic and the neutral salt). The basic glycerophosphate of quinine has the following formula—

$$C_3H_7O_3,PO\begin{matrix}O(C_{20}H_{24}N_2O_2)\\O(C_{20}H_{24}N_2O_2)\end{matrix} + 7H_2O = 944.$$

Practically, the preparation of the glycerophosphate with two molecules of quinine cannot be carried out by the double decomposition of an alkaline glycerophosphate and a salt of quinine. Like all the glycerophosphates, glycerophosphate of quinine must be obtained by precipitation in a dehydrating agent in which it is insoluble, such as ether. By preparing it under these conditions glycerophosphate of quinine takes the form of a very white, light, crystalline powder, unchangeable when exposed to the air, easily soluble in water acidulated with glycerophosphoric acid, soluble in warm water, in strong alcohol in the cold or in dilute warm alcohol, and insoluble in ether. It contains 1 molecule of acid, 2 molecules of quinine, and 7 molecules of water. The neutral glycerophosphate of quinine—

$$C_3H_9PO_6,C_{20}H_{24}N_2O_2 + 10H_2O.$$

is a pale yellow crystalline powder, moist to the touch, having a horny appearance when deprived of part of its water of crystallisation. It melts at 120° into a vitreous

mass of a brownish colour. It is easily prepared by the double decomposition of an alkaline glycerophosphate and a neutral salt of quinine (sulphate or hydrochlorate); but the prolonged washings necessary to rid it of the sulphates or chlorides partly decompose it. Both these glycerophosphates may be estimated by dissolving in a mixture of hot alcohol and water, adding a few drops of phthalein and then a solution of decinormal potash, until the rose-colour remains permanent.

February, 1898.

A New, Very Sensitive, and Specific Reaction of Citric Acid. Detection in Vegetable Juices, Wine, Milk, &c.—G. Denigès.—In a previous communication the author briefly mentioned that the products of oxidation of citric acid, by manganic oxidising agents in an acid medium, gave an insoluble mercurial compound in the presence of mercuric sulphate. On further studying this reaction he finds that it is of extreme sensitiveness, and under certain conditions a specific test for citric acid. The method has been applied to numerous cases with excellent results.

Estimation of Commercial Sulphate of Quinine.—L. Barthe.—A claim for priority by the author over a method described by M. Kubli in the *Mercure Scientifique*, February 1, 1897.

Journal de Pharmacie et de Chimie,
Series 6, vol. vii., No. 8.

The Physiology of Gentianose; its Splitting-up by Soluble Ferments.—E. Bourquelot.—It is well known that the cane-sugar formed in beetroot is, in the second vegetative period, which corresponds to the formation of grains, split up into assimilable sugars (dextrose and levulose) by a soluble ferment. An analogous splitting-up of gentianose in gentian has been shown to take place. Invertine only partially hydrolyses gentianose, while the liquid from *Aspergillus* does it completely.

Criticisms on the Volumetric Methods for the Estimation of the Phosphoglycerates.—H. Imbert and J. Pages.—After reviewing the work of many writers on this subject, the authors conclude:—1st, that the method of estimating the glycerophosphates proposed by MM. Imbert and Anstruc is sufficiently exact for all practical purposes, and can be generally used: 2nd, that—thanks to the use of chloride of calcium—the phosphates can be estimated in the presence of glycerophosphates, especially if the quantity reaches at least 5 per cent of the mixture; below this limit the operation is rather more delicate: 3rd, the boreates and silicates are not detected, and must be specially tested for, qualitatively.

Glycerophosphate of Quinine.—M. Moncour.—Glycerophosphate of quinine can be prepared by neutralising a titrated solution of glycerophosphoric acid by an equivalent quantity of quinine; or by the double decomposition of two solutions, one containing a salt of quinine, and the other glycerophosphate of lime; these solutions are used in equivalent proportions. The compound obtained is the same by both methods, and appears in the form of fine white needles closely resembling sulphate of quinine in appearance. It is inodorous and bitter, but not nearly so bitter as the sulphate. It is hardly soluble in water or cold alcohol, but readily so in hot alcohol and glycerin. The insolubility of glycerophosphate of quinine in water is not a very serious drawback, as the addition of a small quantity of citric or hydrochloric acid entirely overcomes it. This new salt of quinine is not altered in its composition by the dilution of its solutions, nor by heat, but, different from other glycerophosphates, is a very stable body; it melts at 154°. It is a basic salt, with the following definitive formula:—

$$O=P\begin{cases}O.C_3H_7O_2\\OH.C_{20}H_{24}N_2O_2\\OH.C_{20}H_{24}N_2O_2\end{cases}+4H_2O.$$

Corresponding to the following composition:—

Quinine	72·64 per cent.
Glycerophosphoric acid ..	19·28 ,,
Water	0·09 ,,

Its richness in quinine is very near that of the other salts employed therapeutically; it is higher than the neutral salt, which only titrates 59·1 per cent, and is almost equal to the officinal sulphate which titrates 74·31 per cent; it can therefore be prescribed in the same doses, and in the same manner, while the presence of glycerophosphoric acid gives it the extra advantage of providing phosphorus in an easily assimilable condition, capable of accelerating nutrition and combating nervous depression.

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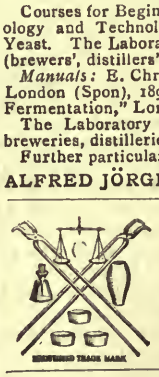

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END OF VOLUME LXXVII.

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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXVIII.—1898.

LONDON:
PUBLISHED AT THE OFFICE, 6 & 7, CREED LANE, LUDGATE HILL, E.C.
AND SOLD BY ALL BOOKSELLERS.

MDCCCXCVIII.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,

6 & 7, CREED LANE, LUDGATE HILL,

E.C.

THE CHEMICAL NEWS.

VOLUME LXXVIII.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2014.—JULY 1, 1898.

ON THE COMPANIONS OF ARGON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

For many months past we have been engaged in preparing a large quantity of argon from atmospheric air by absorbing the oxygen with red-hot copper, and the nitrogen with magnesium. The amount we have at our disposal is some 18 litres. It will be remembered that one of us, in conjunction with Dr. Norman Collie, attempted to separate argon into light and heavy portions by means of diffusion, and although there was a slight difference† in density between the light and the heavy portions, yet we thought the difference too slight to warrant the conclusion that argon is a mixture. But our experience with helium taught us that it is a matter of the greatest difficulty to separate a very small portion of a heavy gas from a large admixture of a light gas; and it therefore appeared advisable to re-investigate argon, with the view of ascertaining whether it is indeed complex.

In the meantime Dr. Hampson had placed at our disposal his resources for preparing large quantities of liquid air, and it was a simple matter to liquefy the argon which we had obtained by causing the liquid air to boil under reduced pressure. By means of a two-way stopcock the argon was allowed to enter a small bulb, cooled by liquid air, after passing through purifying reagents. The two-way stopcock was connected with mercury gas-holders, as well as with a Töpler pump, by means of which any part of the apparatus could be thoroughly exhausted. The argon separated as a liquid, but at the same time a considerable quantity of solid was observed to separate partially round the sides of the tube, and partially beiow the surface of the liquid. After about 13 or 14 litres of the argon had been condensed, the stopcock was closed, and the temperature was kept low for some minutes in order to establish a condition of equilibrium between the liquid and vapour. In the meantime the connnecting tubes were exhausted and two fractions of gas were taken off by lowering the mercury reservoirs, each fraction consisting of about 50 or 60 cubic c.m. These fractions should contain the light gas. In a previous experiment of the same kind, a small fraction of the light gas had been separated, and was found to have the density 17·2. The pressure of the air was now allowed to rise, and the argon distilled away into a separate gas-holder. The white solid which had condensed in the upper portion of the bulb did not appear to evaporate quickly, and that portion which had separated in the liquid did not perceptibly diminish in amount. Towards the end, when almost all the air had boiled away, the last portions of the liquid evaporated slowly, and, when the remaining liquid was only sufficient to cover the solid, the bulb was placed in connection with the Töpler pump, and the exhaustion continued until the liquid had entirely disappeared. Only the solid now remained, and the pressure of the gas in the apparatus was only a few millimetres. The bulb was now placed in connection with mercury gas-holders, and the reservoirs were lowered. The solid volatilised very slowly, and was collected in two fractions, each of about 70 or 80 cubic c.m. Before the second fraction had been taken off, the air had entirely boiled away, and the jacketing tube had been removed. After about a minute, on wiping off the coating of snow with the finger, the solid was seen to melt, and volatilise into the gas-holder.

The first fraction of gas was mixed with oxygen, and sparked over soda. After removal of the oxygen with phosphorus it was introduced into a vacuum-tube, and the spectrum examined. It was characterised by a number of bright red lines, among which one was particularly brilliant, and a brilliant yellow line, while the green and the blue lines were numerous, but comparatively inconspicuous. The wave-length of the yellow line, measured by Mr. Baly, was 5849·6, with a second-order grating spectrum. It is, therefore, not identical with sodium, helium, or krypton, all of which equal it in intensity. The wave-lengths of these lines are as follows:—

Na (D_1)	.. ..	5895·0
Na (D_2)	.. ..	5889·0
He (D_3)	.. ..	5875·9
Kr (D_4)	.. ..	5866·5
Ne (D_5)	.. ..	5849·6

The density of this gas, which we propose to name "neon" (new), was next determined. A bulb of 32·35 cubic c.m. capacity was filled with this sample of neon at 612·4 m.m. pressure, and at a temperature of 19·92 it weighed 0·03184 grm.

Density of neon .. 14·67.

This number approaches to what we had hoped to obtain. In order to bring neon into its position in the periodic table, a density of 10 or 11 is required. Assuming the density of argon to be 20, and that of pure neon 10, the sample contains 53·3 per cent of the new gas. If the density of neon be taken as 11, there is 59·2 per cent present in the sample. The fact that the density has decreased from 17·2 to 14·7 shows that there is a consider-

* A Paper read before the Royal Society, June 16th, 1898.

† Density of lighter portion, 19·93; of heavier portion, 20·01 (*Roy. Soc. Proc.*, vol. lx., p. 206).

able likelihood that the gas can be further purified by fractionation.*

That this gas is a new one is sufficiently proved, not merely by the novelty of its spectrum and by its low density, but also by its behaviour in a vacuum-tube. Unlike helium, argon, and krypton, it is rapidly absorbed by the red-hot aluminium electrodes of a vacuum-tube, and the appearance of the tube changes, as pressure falls, from fiery red to a most brilliant orange, which is seen in no other gas.

We now come to the gas obtained by the volatilisation of the white solid which remained after the liquid argon had boiled away.

When introduced into a vacuum-tube it showed a very complex spectrum, totally differing from that of argon, while resembling it in general character. With low dispersion it appeared to be a banded spectrum, but with a grating, single bright lines appear, about equidistant throughout the spectrum, the intermediate space being filled with many dim, yet well-defined, lines. Mr. Baly has measured the bright lines, with the following results. The nearest argon lines, as measured by Sir W. Crookes, are placed in brackets.

Reds very feeble, not measured.		
First green band,	first bright line	5632·5 (5651 : 5619)
,,	second ,,	5583·0 (5619 : 5567)
,,	third ,,	5537·0 (5557 : 5320)
Second green band,	first bright line	5163·0 (5165)
,,	second ,,	5126·5 (5165 : 5065) brilliant.
First blue band,	first bright line	4733·5 (4879)
,,	second ,,	4711·5 (4701)
Second blue band,	first bright line	4604·5 (4629 : 4594)
Third blue band (first order) ..		4314·0 (4333 : 4300)
Fourth blue band (second order)		4213·5 (4251 : 4201)
Fifth blue band (first order), about		3878 (3904 : 3835)

The red pair of argon lines were faintly visible in the spectrum.

The density of this gas was determined with the following results:—A globe of 32·35 c.c. capacity, filled at a pressure of 765·0 m.m., and at the temperature 17·43°, weighed 0·05442 grm. The density is therefore 19·87. A second determination, made after sparking, gave no different result. This density does not sensibly differ from that of argon.

Thinking that the gas might possibly prove to be diatomic, we proceeded to determine the ratio of specific heats:—

Wave-length of sound in air ..	34·18
,, ,, gas ..	31·68
Ratio for air..	1·408
,, gas	1·660

The gas is therefore monatomic.

Inasmuch as this gas differs very markedly from argon in its spectrum, and in its behaviour at low temperatures, it must be regarded as a distinct elementary substance, and we therefore propose for it the name "metargon." It would appear to hold the position towards argon that nickel does to cobalt, having approximately the same atomic weight, yet different properties.

It must have been observed that krypton does not appear during the investigation of the higher boiling fraction of argon. This is probably due to two causes. In the first place, in order to prepare it, the manipulation of a volume of air of no less than 60,000 times the volume of the impure sample which we obtained was required; and in the second place, while metargon is a solid at the temperature of boiling air, krypton is probably a liquid, and more volatile at that temperature. It may also be noted that the air from which krypton has been obtained had been filtered, and so freed from metargon. A full account of the spectra of those gases will be published in due course by Mr. E. C. C. Baly.

* June 16th. After fractionation of the neon, the density of the lightest same had decreased to 13·7.

THE SPECTRUM ANALYSIS OF SEVERAL NON-CONDUCTING MINERALS BY MELTED SALTS, AND REACTIONS OF THE ELEMENTS.

By A. DE GRAMONT.

I NOW give a few applications of the method I have had the honour of explaining in a previous communication (*Comptes Rendus*, April 18, 1898), by which we are enabled to obtain the spectra of the lines of the elements contained in non-conducting minerals or precipitates, by exposing them, powdered and melted with an alkaline carbonate, to the action of the condenser spark.

Lithium, when tried for by using carbonate of soda, is excessively sensitive; when present even in only very faint traces it is detected by its red line 670·8, and the orange line 610·4, which may also be obtained directly in the cold by causing the condenser spark to strike on a morsel of triphane or of lepidolite.

Sodium is shown by the double red and the less refrangible double green, which will indicate quantities between 0·01 and 0·001; the double line D is always to be seen, either because of its presence in the melted salt or in the substance under examination.

Potassium is scarcely sensitive to this process. It is recognised principally by its green group, Kα 583—578, and by its violet line 404·6, which is less characteristic, but gives a better reaction.

Rubidium, when in unweighable traces, is easily recognisable by its two violet lines 421·6 and 420·2.

Cæsium is equally sensitive by its blue lines 459·3 and 455·6.

The alkaline-earthy metals are especially easy to detect, even in very small quantities, by their principal lines, the last to disappear in the spectra; these lines are—for *calcium*, in the blue 445 5, 443·5, 442·6, and above all in the violet 442·7, as well as 396·9 and 393·4 in the ultra-violet; these last three lines we know correspond with the lines G, H, and K in the solar spectrum; for *strontium* in the blue 460·8, in the indigo 430·6, and in the violet 421·6; for *barium* in the red and orange 649·7 and 614·2, in the green 577·8, 553·6, 493·4, and in the blue 455·4.

Magnesium is recognised with great facility by the green triplet Mgα, which is very well known, and *glucinum* by the blue line 457·3, easy to see, but of considerably less delicacy.

Manganese, which by the direct method of analysis is not to be found, even in minerals with a metallic lustre, such as Haussmannite, is easily detected with the melted salts by its group of five blue lines, Mnα 482—475. The same is the case with *chromium*, which is well characterised by its triple green line 520·9, 520·6, and 520·5, the two latter being difficult to separate with a medium dispersion.

Iron and *nickel*, on the contrary, should not be sought for by this method, and if their lines are not observed it must not be concluded that the metals are not present in the body under examination.

Aluminium, the research of which is as a rule discouraged in text-books by spectrum analysis, has, on the contrary, given me a good reaction by means of its double red line 624·5, 623·5, which is brought out with great distinctness by a very small quantity of alumina in the presence of carbonate of lithium, which in this case is much preferable to the salt of soda.

Vanadium, which gives its spectrum as easily in the melted salts as in the minerals which they dissolve, shows principally by a group of strong lines in the indigo, of

which the least refrangible, 440·8, is the most persistent and the most sensitive, and which extend to 438·0.

Zirconium is easily recognised by its group of five lines between 481·6 and 469·0 in the blue; amongst these 474·0 is the strongest, and the last to disappear.

I will not dwell on the spectra of the lines of the metalloids already described in previous papers, in which I described my researches on the minerals, or in the melted salts. I will only observe that their sensitiveness, which is very great in the compounds in which they are not combined with oxygen,—such as the sulphides, selenides, tellurides, chlorides, bromides, iodides,—becomes, on the contrary, much more feeble in the corresponding oxy-salts, of which the dissociation requires a strong condensation (four to six jars) to cause the appearance of the lines of the metalloids. In this case the use of carbonate of sodium seemed to give me better results than carbonate of lithium. A certain number of minerals examined by this method have enabled me, by means of the spectral reactions I have just described, to diagnose the following elements:—

Orthose-adulaire, from Saint-Gothard and from Grisons: silicon, aluminium, potassium, sodium, barium, calcium, and sometimes magnesium.

Orthose-cassinite, from Blue Hill, U.S.A.: the same spectra, but the barium was much more developed and without magnesium.

Albite, from Modane: silicon, aluminium, sodium, calcium, magnesium.

Albite peristerite, from Villeneuve, Canada: the same spectra, with the calcium more developed.

Oligoclase, from Bakersville, U.S.A.: silicon, aluminium, sodium, calcium, barium. From Ytterby, Sweden: the same spectra, but less barium, and a stronger principal line of strontium 421·6.

Labradorite, from the coast of Labrador: silicon, aluminium, sodium, calcium.

Anorthite, from Somma and from New Caledonia: silicon, aluminium, sodium, calcium, and magnesium. The spectrum of calcium is much more developed and more brilliant than in the case of the other plagioclases, by which it is possible to distinguish anorthite at the first view of the whole spectrum.

Petalite, from Uto, Sweden: by Na_2CO_2, silicon, lithium, calcium, rubidium, aluminium (seen better with Li_2CO_3).

Pollux, from Hebron, U.S.A.: by Na_2CO_3, silicon, cæsium, lithium, calcium; and with Li_2CO_3, aluminium and sodium.

Rhodonite, from the valley of Louron, Hautes-Pyrenees: silicon, manganese, calcium, aluminium.

Beryl, from Limoges: silicon, aluminium, sodium, glucinum, calcium.

Spessartine garnet, from Saint-Marcel, Piedmont: silicon, aluminium, manganese, calcium.

Zircon, from Miask, Oural: silicon, zirconium, aluminium, calcium.

Axinite, from Oisans: silicon, aluminium, calcium, manganese, magnesium.

Garnierite (pale green), from Kanala, New Caledonia: silicon, magnesium, aluminium, but no lines of nickel, though this metal is present to the extent of 3 or 4 per cent.

Sphene, from Zermatt: silicon, calcium, titanium, aluminium.

Aerinite, from Caserras, Aragon: silicon, calcium, aluminium, magnesium, barium, vanadium.

Calc-spars: several among these have given the green triplet of magnesium and some of the lines of strontium, as well as the complete spectrum of the calcium lines.

Celestine, from Sicily: strontium, barium, sulphur with difficulty.

Siderochrome, from Silesia: chromium, magnesium, calcium. From Brousse, Asia Minor: the same spectrum and also silicon, aluminium, sodium.

Blende, from Santander and Pierrefitte: zinc, sulphur, and sometimes silver, cadmium, calcium, aluminium.

Cryolite, from Greenland: melted by itself, without the addition of any other salt, aluminium, sodium, lithium, silicon, magnesium, calcium.

This method, as can be seen, gives satisfactory results with most simple bodies, but with unequal sensitiveness. When necessary the spectrum under examination can be simplified by reducing the condenser to one jar, which will only allow of the principal lines of the metals being seen.—*Comptes Rendus*, cxxvi., No. 21, May 23, 1898.

ON THE

ANALYSIS OF BONE SUPERPHOSPHATE.

By F. POQUILLON.

The analysis of bone superphosphates is made, officially, in the same manner as that of mineral superphosphates. We estimate the phosphoric acid soluble in water, the phosphoric acid soluble in citrate of ammonia, and the total phosphoric acid.

We simply admit that the bone superphosphate should contain a higher proportion soluble in water than the mineral does, but no figures are given to show that this is the case. As a matter of fact, there is no reason for this at all, the proportion soluble in water varies with the quantity of sulphuric acid used in its manufacture; no matter whether it is bone or mineral superphosphate.

The only criterion used in deciding whether a superphosphate is bone or mineral is the estimation of the nitrogen. But this estimation does not allow of the detection of adulteration. As a matter of fact, a nitrogenous substance can easily be added to a mineral superphosphate or to a superphosphate of bone-ash to make it appear as a genuine bone superphosphate. We have recently endeavoured to find a method of controlling the estimation of nitrogen in this respect, and the following is the method we propose.

Method by the Estimation of the Fatty Matter.

This method consists in determining in a superphosphate the amount of fatty matter soluble in sulphide of carbon or in benzene, and in calculating the relation between this figure and the quantity of phosphoric acid present. This proportion is practically constant in bone superphosphates.

Green bones always have the fat removed before being transformed into superphosphates. The removal of the fat is done by two methods; by water and by benzene. Two experiments, made with each of these methods, have given the following results:—

	Total P_2O_5 per cent.	Fatty matters dissolved in benzene.	
		Per cent in bone.	Per cent P_2O_5 total.
1.	17·31	0·58	3·35
2.	17·37	0·66	3·80
Means ..	17·34	0·62	3·58

But, and here is the most important point of our method, when we treat bones from which the fat has been removed even with benzene, with sulphuric acid to transform them into superphosphates, fatty bodies are set free which are dissolved by a fresh treatment with sulphide of carbon.

We now give the results of four experiments on bone superphosphates which had had the fat removed by benzene and had then been treated with sulphide of carbon.

	P_2O_5 per cent total.	Fatty matter dissolved.	
		Superphosphate per cent.	P_2O_5 per cent total.
1.	17·10	1·14	6·67
2.	20·50	1·19	5·81
3.	17·35	1·16	6·68
4.	17·35	1·12	6·46
	19·07	1·45	6·36

If we exhaust a degelatinised bone superphosphate, from bones which have had the fat removed by water, with sulphide of carbon, we find, in addition, the fatty matter which the water has left in the bones; that is to say—

Superphosphate .. 1·15+0·62=1·77 per cent
Total P_2O_5 .. .. 6·36+3·58=9·94 „

Direct determinations of the bone superphosphates generally met with, in France at least, made from bones from which the fat has been removed by water, give the following results:—

	Total P_2O_5 per cent.	Fatty matters. Superphosphate per cent.	Fatty matters. Total P_2O_5 per cent.
1. ..	17·80	2·04	11·40
2. ..	17·80	2·08	11·68
3. ..	18·40	2·24	12·71
4. ..	16·80	1·74	10·40
5. ..	16·90	1·82	10·76
6. ..	16·90	1·96	11·59
Means .	17·43	1·98	11·36

In working a superphosphate from green bones, which are also called "dissolved bones," the reaction is the same; it being, of course, understood that the fat has been removed from the bones before they are transformed into superphosphates; this should always be done commercially. In England, however, where a large quantity of dissolved bone is manufactured, the fat is not always removed; but in such cases it is bone from La Plata, the West Indies, or other tropical countries that is used, such bone rarely containing more than a trace of fat.

A direct estimation of green bones from which the fat has been removed, treated with sulphuric acid, gave the proportion of 9·68 of fatty matter per cent of the total P_2O_5.

We thus see that the proportion 10 to 12 of fat per 100 of phosphoric acid is characteristic of a superphosphate of green bones, or bones which have been degelatinised, after having originally had the fat removed by water.

The proportion 6·5 per cent is characteristic of a superphosphate from bones from which the fat has been removed by benzene.

A proportion of over 12 would indicate a superphosphate from bones from which the fat had not been removed.

From the point of view of adulteration, it may be asked if it is not possible to find a nitrogenous matter which, when added to a mineral superphosphate, could at the same time supply the necessary fat to make the characteristic proportion 10 or 12, as described above.

To decide this point, we have estimated the proportion of fatty matter in the more common nitrogenous substances and have obtained the following results:—

Material used.	Nitrogen per cent.	Fatty matters. Without treating with H_2SO_4. Per cent material.	Without treating with H_2SO_4. Per cent nitrogen.	After treating with H_2SO_4. Per cent material.	After treating with H_2SO_4. Per cent nitrogen.
Green horns . ..	10·94	0·58	5·30	0·39	3·56
Dried horns, No. 1	14·08	1·20	8·52	0·82	5·82
„ No. 2	13·73	0·97	7·07	0·79	5·75
Dried blood, No. 1	11·25	0·56	4·98	0·39	3·46
„ No. 2	12·65	0·45	3·56	0·37	2·93
Dried leather . ..	7·20	0·73	10·14	0·56	7·78

It will be seen from the above table that the use of these materials for the purpose of adulteration is impossible. In fact a bone superphosphate 16/18 contains from 0·75 to 1·0 per cent of nitrogen. If we take the nitrogenous matter containing the highest proportion of fat, viz., dried leather, which contains 10·14 of fatty matter per 100 of nitrogen, it is evident that to obtain 0·75 of nitrogen we have only to add $\frac{0{\cdot}75 \times 10{\cdot}14}{100} = 0{\cdot}076$ of fatty matter, while bone superphosphate contains $\frac{16 \times 11}{100} = 1{\cdot}76$.

We cannot, therefore, obtain a superphosphate containing at the same time 0·75 per cent of nitrogen and 1·76 per cent of fatty matter without using very exceptional nitrogenous material, or by adding fatty matter quite apart. Further, so small a quantity of fat (1·76 per cent of the superphosphate) could not be properly mixed in a homogeneous manner. We therefore think that our method, without being absolutely correct, will generally serve to detect cases of adulteration. — *Moniteur Scientifique*, Series 4, vol. xii., June, 1898.

THE DETERMINATION OF THE REDUCIBILITY OF IRON ORES.

By T. WIBORGH.

At the last International Congress for the unification of the methods adopted for the commercial assay of various materials, Professor J. Wiborgh, of the School of Mines at Stockholm, presented a paper on a method for the valuation of the degree of reducibility of iron ores. The following is a *resumé* of this paper:—

In the blast-furnace the reduction of an iron ore is effected both by carbon and by carbonic oxide, and it is necessary to be able to distinguish between those minerals which are easily reduced and those which are not. The former can be brought to a state of fusion with a much smaller expenditure of fuel than the latter, and this difference is largely due to the greater or less facility with which the ore gives up its oxygen to the reducing agent (carbon or carbonic oxide). This characteristic of greater or less oxidation may be compared with the greater or less ease with which carbon under different forms burns in air, — such as diamond, graphite, coke, charcoal, &c. While the combustion of diamond requires a very high temperature, the combustion of wood charcoal is, on the contrary, effected with great ease, and, as a matter of fact, takes place at a relatively low temperature. In the one case, as with the other, the difference may be ascribed to the difference in molecular structure. The density of the molecule increases with its crystalline form, the iron ore will be less easily reduced, and the carbon will be more difficult to burn, when the two substances occur in a very compact form. Furthermore, it has long been known as an accepted fact, with regard to minerals of the same degree of oxidation, that the reducibility varies inversely with the specific gravity. Any treatment which has for its object the diminution of the specific gravity is equally of value in increasing the reducibility, and it is well known that a pulverulent ore is much more easily reduced than one in compact lumps. A previous roasting, for instance, which results in the elimination of certain substances—such as water, organic matter, carbonic acid, and sulphur—also increases the reducibility of the ore by decreasing its compactness. This roasting, therefore, makes the hydrated, carbonated, and magnetic ores more easily reducible. If the peroxide of iron is more easily reduced than the magnetic oxide, it is on account of the fact that a body originally containing more oxygen gives up a part of it with greater ease. It thus follows that this first loss of oxygen breaks up the molecular structure of the substance (in the case of an ore this is obvious), and thereby its reducibility is increased. Of two ores, one of which is a peroxide and the other a suboxide of iron, the former will always be more easily reduced than the latter. The peroxide, further, possesses the property of dissociating the carbonic

oxide, though under conditions which have not yet been exactly defined.

It stands to reason that, though chemical analysis enables us to determine the exact composition of an iron ore, it does not, on the other hand, supply us with any practical indication as to the greater or less ease with which such an ore will be reduced in the blast-furnace. From as far back as the year 1884 the author has been elaborating a method which had for its object the determination of this important characteristic; but this research was stopped until 1895, at which time it was taken up again at the School of Mines at Stockholm, under the direction of David Johanssen.

The apparatus used is composed of a generator of circular section, with a diameter of 0·25 metre and a height of 1·20 metres, in which an iron tube is suspended, having an internal diameter of 50 m.m.; in this tube, through which the gas from the generator passes, the samples of ore to be assayed are placed, and left there for a known time. Wood charcoal, burnt on a grate without forced draught, is the fuel used. The products of combustion are carried off by means of a pipe leading to the flue, the air entering below the grate. The actual reduction-tube terminates with a narrow end of about 35 m.m. diameter. This reduction-tube is protected from the flame by means of fire-clay; its total length is 1·60 metres, and its lower extremity is at a distance of about 250 m.m. from the hearth.

The sample of ore is crushed, and must pass through a sieve of 16 meshes per square centimetre. It is then placed in a boat of wire gauze, and suspended in the tube by means of a metallic wire. We first used 30 to 40 grms. of the mineral, but later on we made use of smaller boats not containing more than 8 or 10 grms. of the ore, three of these being placed in a larger boat at the same time. By this means several ores could be treated at one time, and comparisons made with any typical sample of iron ore.

The estimation of the temperature at which reduction takes place can be made by means of fusible alloys, or by using a thermophone invented by the author (*Chemiker Zeitung*, xx., p. 209, 1896). At 500 m.m. from the upper end of the tube the temperature is 400° C.; at 900 m.m. it is 525° C.; at 1200 m.m. it is 700° C.; and at 1500 m.m., from the same point, it is from 800° to 880° C. The proportion of carbonic acid present in the reducing gas varies from 3·2 to 3·6 per cent, and the proportion of carbonic oxide is about 30 or 32 per cent. The proportion between the CO_2 and the CO remains practically equal to 0·1. If the lower end of the tube is raised by 350 m.m. from the furnace, the proportion of carbonic acid in the gas is increased to 17 per cent.

The assay may be carried out in two distinct manners,—by allowing the boat to gradually descend to the warmest part, or by placing it there at once. But as it is necessary to take into account the separation of the carbon which occurs at about 400° by dissociation of the reducing gas, and as, on the other hand, this dissociation is of considerable importance in the reduction of the mineral, it is preferable to adopt the former method. We can also—and this is an excellent plan—leave the ore at a temperature of 400° for one hour, and then lower the boat directly into the hottest part of the tube, where it can be left for another hour. The experiments which will be described further on were conducted in this manner.

When the reduction is complete it is necessary to be careful to allow the boats to cool in a current of carbonic oxide, so as to prevent the re-oxidation of the metallic iron obtained. There then remains the analysis of the reduced ore to be done, and this will offer considerable difficulty if the reduction has not been complete, or if the metallic iron is mixed with oxide.

The possible proportion of oxygen remaining in the ore after reduction is calculated under the *term*, *degree of oxidation of the iron*. This degree of oxidation is the proportion (in units per cent) of the oxygen found after reduction, to the amount of oxygen which would be found if the whole of the iron present was in the state of peroxide. Under such conditions we take *the degree of oxidation* of peroxide of iron to be 100, that of the magnetic oxide 88·9, and that of the suboxide 66·7. Finally, it must be borne in mind that the quantity of carbon present in the ore, after reduction, must be estimated. The characteristics, therefore, to determine are:—(1) carbon; (2) total iron; (3) metallic iron; (4) degree of oxidation.

A. *Estimation of the Carbon.*

For this purpose we use Särnström's apparatus as used for the estimation of the carbon in cast-iron. The oxidation is carried out by the chromic solution, and the absorption of the carbonic acid by means of potash.

B. *Estimation of the Metallic Iron.*

The reduced sample is treated with sulphuric acid, and the hydrogen collected. The measurement of the volume of the gas will enable one to calculate the metallic iron present. For this estimation we make use of a large-sized test-tube, in which is placed from 0·2 to 1·0 grm. of the sample, according to whether it is more or less completely reduced. This tube must be closed by means of an indiarubber stopper pierced with two holes, through which pass respectively the tube of a funnel and an escape-tube. The funnel is used for the admission of sulphuric acid. The escape-tube is for the purpose of leading the hydrogen given off to a potash wash-bottle, in which all traces of carbonic acid gas which might be present, if the ore had been insufficiently roasted, would be absorbed. After this washing, the hydrogen passes into a graduated burette, of which the lower extremity is connected to a hot-water oven. The sample is first placed in the test-tube, a little water is then added, and the cork inserted. The exact level must now be established between the water oven and the burette, after which exactly 10 c.c. of dilute sulphuric acid (one part of acid to eight parts of water) is run into the test-tube. When the reaction appears to be finished the test-tube is warmed and kept at the boiling-point for a few moments. The level must now be again adjusted, the burette cooled down to 20° C. (this should also have been done at the commencement), and the volume of the gas read off, from which the quantity of acid introduced may be calculated. All these details are not actually insisted upon, but they will always be found worth notice in a gas analysis.

The reaction which takes place is the following:—

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Now 1 litre of hydrogen at 0° C., at a pressure of 760 m.m. of mercury, weighs 0·08957 grm.; therefore 1 grm. of iron will give $\frac{2 \times 0{\cdot}1 \times 1000}{56 \times 0{\cdot}08957} = 39{\cdot}8$ c.c. of hydrogen at a temperature of 0°, and at the normal pressure. At 20° C. the volume of the hydrogen will be 42·7 c.c.

This figure has further been verified experimentally by the use of samples of iron containing variable amounts of carbon. The following are the results obtained:—

0·1 grm. of iron with 0·08 per cent of carbon gave 42·4 c.c. of hydrogen.
0·1 grm. of iron with 0·34 per cent of carbon gave 41·4 c.c. of hydrogen.
0·1 grm. of iron with 0·78 per cent of carbon gave 41·2 c.c. of hydrogen.
0·1 grm. of iron with 3·80 per cent of carbon gave 34·8 c.c. of hydrogen.

From the above it may be seen that with irons containing a high percentage of carbon the gaseous volume is distinctly diminished, because of the formation of carbides of hydrogen. But as a matter of fact this particular point has not much bearing on the class of assays with which we are now concerned, since the iron reduced by the method just described would never contain more than

a trace of carbon. The only loss of hydrogen which might occur would be caused by the action of this gas on the ferric salt in solution (*i.e.*, by the formation of the ferrous salt and water).

C. *Estimation of the Total Iron.*

0·25 grm. of the sample is attacked with hydrochloric acid, filtered, and transformed into sulphate by evaporation with sulphuric acid. This is taken up with water, reduced by the action of zinc, and the iron titrated with permanganate.

D. *Determination of the Degree of Oxidation.*

0·4 of the sample is placed in an emery-stoppered test-tube, having only a very small orifice. To begin with about 5 c.c. of a 10 per cent solution of sulphuric acid is added, and the whole left at the ordinary temperature, but frequently shaken. Complete solution takes from thirty to sixty minutes. When all disengagement of gas has ceased, about 5 c.c. of sulphuric acid, of 1·23 density, are added, and the solution warmed until the whole of the iron is dissolved. This solution is then poured into a beaker and titrated with permanganate.

In the case of refractory ores which are not easily attacked, the first liquor obtained by the action of the dilute acid must be separated by decantation, and the undissolved residue submitted to a fresh attack by a more concentrated acid. The two solutions must then be added together for titration. Having thus obtained the whole of the iron contained in the sample of the ore, and having determined by the preceding assays the quantity of metallic iron and the quantity of iron in the state of suboxide, it is a matter of comparative simplicity to calculate the degree of oxidation. Thus let n % be the total iron present, and r % the proportion of metallic iron, and m % the quantity of iron present in the state of suboxide, then the degree of oxidation is arrived at by means of the following formula:—

$$\frac{\frac{(n-r)\,3}{2}}{m-r} + \left[\frac{(n-r)-(m-r)}{2}\right]3 = \frac{100}{x},$$

from which we get:—

$$x = \text{the degree of oxidation} = 1 - \frac{\frac{m-r}{3(n-r)}}{100}.$$

The formula for the peroxide of iron, Fe_2O_3, may very well be written Fe_6O_9. It can be shown that this compound may successively lose 4 molecules of oxygen, which will correspond to the following four different oxides:—

	Degree of oxidation.
$3Fe_2O_3 = Fe_6O_9$	100·0 oxide.
$3Fe_2O_3 - O = Fe_6O_8$ ..	88·9 suboxide of the oxide.
$3Fe_2O_3 - 2O = Fe_6O_7$ ..	77·8 oxide of the suboxide.
$3Fe_2O_3 - 3O = Fe_6O_6$..	66·7 suboxide.

E. *Determination of the Degree of Reduction.*

The real estimation of the reducibility is given by the *degree of reduction*,—that is to say, by the relation between the iron reduced and the total iron present (in units per cent).

The experiments which have been carried out by the method above described, on thirty-six samples of ores, have shown that the peroxidised minerals are more easily reduced than those of the magnetite class. This difference has, however, long ago been established in practice. But there is another point which must not be lost sight of,—that these experiments on the reducibility of iron ores also show that the oxidation point may vary in a marked degree. And it may well be hoped, from the above-mentioned facts, that a simple and practical method for the rapid evaluation of the comparative reducibility of any iron ore may be easily arrived at.

It must be taken as an established fact that between peroxide of iron and metallic iron there exists a complete series of intermediary states, which are, and must be, determined by the action of the reducing agents. To particularise, the existence of the suboxide of the oxide ($Fe_3O_4 = Fe_6O_8$), of which the degree of reducibility is 88·9, was shown by Ackerman in the year 1882. Still more important, from the point of view of reduction, is the oxide of the suboxide, Fe_6O_7, of which the existence was shown by Wedding. The degree of oxidation of this body is 77·8.

From a careful consideration of all the experiments carried out by the author, the following conclusions may be drawn:—Every mineral giving a degree of oxidation of 77·8, at a low temperature, will be easily reducible,—that is to say, it can be transformed into metallic iron by the ordinary furnace gas. This degree of oxidation corresponds to a particular and definite molecular condition, by reason of which there is not a particle of metallic iron formed until it has been reached. As soon, however, as this point *has* been reached the reduction proceeds very rapidly, at the same time *the degree of oxidation* diminishes, but, contrary to the belief of most metallurgists, the suboxide or the protoxide of iron does not constitute a "molecular step" in the reduction of the ore.—*Moniteur Scientifique*, Series 4, vol. xii., June, 1898.

DETERMINATION OF TEMPERATURE BY MEANS OF THE DATA GIVEN IN A CHARLOTTENBURG CERTIFICATE.

By A. W. WARRINGTON, M.Sc.

ALTHOUGH it must be pretty generally known in England that thermometers obtained from Germany may, for a few extra shillings, be examined at Charlottenburg and furnished with a certificate giving, to the one-hundredth of a degree, the corrections to be applied at various points, I doubt whether we sufficiently avail ourselves of this privilege, or are aware of the extreme trustworthiness of results obtained by use of such a certificate.

A thermometer, designated in this paper by T 9591, made of normal Jena glass and divided into tenths of a degree, was examined by me after the manner recommended by M. Guillaume in his "Traité Pratique de la Thermométrie," its fundamental interval being determined by comparison at several points with a thermometer, T 11806, made by Tonnelot and examined at the Bureau International des Poids et Mesures.

T 9591 was furnished with a Charlottenburg certificate, by means of which its readings might be reduced to those of the standard gas thermometer at Charlottenburg. This standard is, for the purpose of this paper, treated as identical with the "Paris" hydrogen standard.

To use the Charlottenburg certificate, the zero of the thermometer, after prolonged exposure to the temperature of the room, should be determined. Let the zero be x; then, if the thermometer be used in a vertical position and the whole of the column of mercury be exposed to the temperature to be measured, the following, according to the Charlottenburg certificate, are the only corrections which need be applied to reduce the readings of T 9591 to the standard gas thermometer.

At 0°	add $-x$
,, 10°	,, $-x-0{\cdot}02°$
,, 20°	,, $-x-0{\cdot}02°$
,, 30°	,, $-x-0{\cdot}05°$
,, 40°	,, $-x-0{\cdot}01°$
,, 50°	,, $-x-0{\cdot}04°$

The corrections for intermediate temperatures being determined by Broch's method of interpolation.

The comparisons given in the accompanying table

$-x$.	T 9591 unreduced.	T 9591 reduced by Charlottenburg certificate.	T 9591 reduced by method employed at Sèvres.	Th.* obtained from T 11806.	Charlottenburg −Th.*	Sèvres −Th.*
+0·161	14·2575	14·3985	14·3963	14·3945	+0·004	+0·0018
+0·161	37·0062	37·1462	37·1490	37·1472	−0·001	+0·0018
+0·161	25·4190	25·5410	25·5497	25·5501	−0·009	−0·0004
+0·161	29·7695	29·8805	29·8834	29·8877	−0·007	−0·0043
+0·161	40·8040	40·9530	40·9485	40·9473	+0·006	+0·0012
+0·140	9·6215	9·7445	9·7486	9·7490	−0·005	−0·0004
+0·140	9·028	9·150	9·1574	9·156	−0·006	+0·0014
+0·140	8·038	8·162	8·1640	8·163	−0·001	+0·0010
+0·140	6·388	6·515	6·5193	6·516	−0·001	+0·0033
+0·140	4·7188	4·8488	4·8448	4·8444	+0·004	+0·0004
				Probable error of a determination	±0·004	±0·0014

* Th = T according to the hydrogen standard at Sèvres.

illustrate the method and the degree of accuracy obtainable.

In conclusion, the Charlottenburg certificate costs only a few shillings; by its means reductions are made with the greatest ease, and, if the bore of the thermometer is a good one, the reductions are correct to 0·01°.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 16th, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Edward Gardner, 27, Thurlow Road, Hampstead, N.W.; Henry J. S. Sand, 2, Cantlowes Road, Camden Square, N.W.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

Harry Brearley; Arthur William Cowburn; Charles W. Tisdale Davies; Edwin Dowzard; A. Grant Russell Foulerton; Oswald Hamilton; A. Stanley Hemmy, B.A., M.Sc.; Robert Findlay Hislop; George Arthur Jarvis; Harry Lancelot Lee; William Lewins, B.Sc.; George Herbert Martin, B.A.; Charles James Meads; Leonard Myddleton Nash; Alex. MacGillivray Neilson; Edward John Russell, B.Sc.; Matthew Joseph Sheridan; Sigmund Stein, Ph.D.; Oscar Julian Steinhart, Ph.D.; Samuel Auchmuty Tucker, Ph.B.; Henry Trench Waller; Frank Edwin Weston; Edmund Thomas Whitaker, B.Sc.; William Ernest Wild, B.Sc.; William Williamson; Ernest Witham; Charles Arthur Wrench.

Of the following papers those marked * were read:—

*86. "*Preparation of a Standard Acid Solution by Direct Absorption of Hydrogen Chloride.*" By G. T. MOODY.

A very rapid and accurate method of preparing a standard acid solution consists in absorbing hydrogen chloride in water, determining the resulting increase in weight, and subsequently diluting to a suitable bulk. The absorption is conveniently carried out in a conical glass flask, having a capacity of about 80 c.c., and closed by a glass stopper. Through the stopper pass two tubes, one of which reaches nearly to the bottom of the flask and serves for delivery of the gas. From 2 to 4 grms. of the gas may be absorbed in 40 c.c. of water in three minutes, and if the necessary apparatus for generating hydrogen chloride is kept fitted, a standard acid solution can be prepared in less than fifteen minutes.

*87. "*Researches on the Terpenes.* III. *Halogen Derivatives of Fenchene and their Reactions.*" By JOHN ADDYMAN GARDNER, M.A., and GEORGE BERTRAM COCKBURN, B.A.

The authors give a further account of the properties of chlorofenchenephosphonic acid, $C_{10}H_{14}Cl\cdot PO(OH)_2$ (*Trans.*, 1897, lxxi., 1156), and describe the halogen derivatives of fenchone produced during its formation. The first action of phosphorus pentachloride on fenchene results in the replacement of the oxygen atom by chlorine, and production of two isomeric liquid substances, termed α- and β-chlorofenchene hydrochloride. These two isomerides cannot be separated by fractional distillation, but distil together at 105—110° under 16 m.m. pressure. The α-isomeride is, however, very much the less stable of the two, and loses hydrogen chloride very readily, even when distilled with steam, producing chlorofenchene. The β-isomeride is much more stable towards reagents, and does not lose hydrogen chloride by boiling with aniline; this elimination can be effected, however, by prolonged heating with zinc dust and glacial acetic acid, and chlorofenchene is obtained. Unlike the chlorocamphene hydrochlorides, β-chlorofenchene hydrochloride is completely decomposed by warming with strong sulphuric acid, and yields no substance analogous to camphenol.

Chlorofenchene, $C_{10}H_{15}Cl$, is a crystalline substance very like chlorocamphene in appearance. It boils at 80—83° under 16 m.m., and at 190—192° under the ordinary pressure. It is very soluble in alcohol, ether, benzene, light petroleum, chloroform, and carbon disulphide, the vapour of the last being sufficient to liquefy it. It has a specific rotatory power of $[\alpha]_D = +35{\cdot}92°$. Chlorofenchene slowly reacts with phosphorus pentachloride, and chlorofenchenephosphonic acid is formed on treating the product with water.

When sodium chlorofenchenephosphonate is treated with bromine water, it is decomposed quantitatively into sodium phosphate and *chlorobromofenchene*, $C_{10}H_{14}ClBr$; this is a colourless oil which boils at 113—114° under 11 m.m., but decomposes on boiling under atmospheric pressure. It has a specific gravity of 1·38039 at 16°, and a specific rotatory power of $[\alpha]_D = -8{\cdot}42°$. The halogen atoms cannot be eliminated by heating with aniline, with zinc dust and glacial acetic acid, or with sodium in methylic alcohol solution.

*88. "*Researches on the Terpenes.* IV. *On the Oxidation of Fenchone.*" By JOHN ADDYMAN GARDNER and GEORGE BERTRAM COCKBURN.

Fenchone is much more stable towards oxidising agents than camphor, but when oxidation does take place a much more complete breaking down of the molecule occurs. The authors have oxidised fenchone by prolonged heating on the water-bath with concentrated nitric acid (sp. gr. 1·4). The action was very slow, and after heating for a week, they found that only about 50 per cent of the ketone had been attacked. Isocamphoronic acid, dimethyltricarballylic acid, dimethylmalonic acid, isobutyric acid, acetic acid, and nitrofenchone were isolated from the product of oxidation.

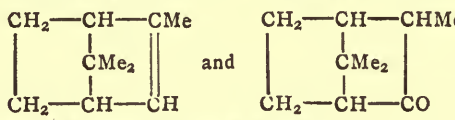
The isocamphoronic acid crystallised from ether and ethylic acetate in tabular plates melting at 163—164°, and is identical with the isocamphoronic acid obtained by Tiemann from campholenic acid. The yield was

about 1·5 per cent of the weight of the fenchone actually oxidised.

The dimethyltricarballylic acid melted at 155°, and on treatment with acetic chloride gave an anhydride melting at 139—141°. The triethylic salt was a colourless liquid and boiled at 172—174° under 19 m.m. pressure. The lead salt, $(C_8H_9O_6)_2Pb_3$, was an insoluble powder. The yield of this acid was 30 per cent, and of dimethylmalonic acid 4 per cent of the fenchone oxidised.

Nitrofenchone is a colourless oil which distils at 146—151° under 14 m.m. pressure, and on reduction with stannous chloride is converted into an amine.

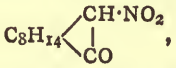
The authors are of opinion that if Bredt's formula be accepted for camphor, these results, taken together with the production of camphopyric acid from fenchene without the intermediate formation of camphoic acid, and from camphene, are sufficient to establish the formulæ—



for fenchene and fenchone respectively.

*89. "*Nitrocamphor and its Derivatives.* Part I. *Isodynamic Forms of Nitrocamphor.*" By T. M. LOWRY, B.Sc.

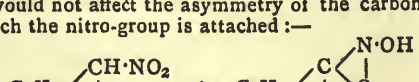
Although, theoretically, it should be possible to obtain two stereoisomerides of a compound represented by the formula—



it appears that only one (the α') of the two possible forms of nitrocamphor is produced under all ordinary conditions, since the various substances described as isomeric nitrocamphors have been found by the author to have the same properties when sufficiently purified.

The product obtained by heating nitrocamphor (*Proc.*, 1897, xiii., 169) has the formula $C_{20}H_{28}N_2O_5$, and is identical with a substance already described by Cazeneuve as nitrosocamphor (*Bull. Soc. Chim.*, 1888, iii., I., 558); it appears to be an *anhydride* formed by the removal of the elements of a molecule of water from two molecules of nitrocamphor, or rather of an isodynamic form of the latter which may be termed pseudonitrocamphor. This view finds support in the fact that the anhydride, like the salts formed from nitrocamphor, is strongly dextrorotatory, whereas nitrocamphor is lævorotatory; and that when heated or acted upon by alcoholic potash, it breaks up into camphorquinone and nitrous oxide, undergoing a change analogous to that which Nef has shown to take place on acidifying a solution of sodium ψ-nitroethane (*Annalen*, 1894, cclxxx., 263).

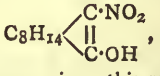
If pseudonitrocamphor be represented by a formula corresponding to that which Hantzsch and Schultze have assigned to pseudophenylnitromethane, rather than by an isonitro-formula such as Nef has proposed, it is obvious that the conversion of nitrocamphor into the isodynamic form would not affect the asymmetry of the carbon atom to which the nitro-group is attached:—



The author considers that important evidence of the independent existence of pseudonitrocamphor is afforded by the fact that solutions of nitrocamphor exhibit the phenomenon of multirotation hitherto observed only in the case of carbohydrates. This is true of πα'-bromonitrocamphor, in which the group $-CH(NO_2)\cdot CO-$ is also present, but not of α'α-nitrochlorocamphor, α'α-nitrobromocamphor, nor of the anhydride or salts obtained from nitrocamphor, from all of which the hydrogen atom contiguous to the nitro-group has been eliminated. The extent to which the rotatory power of nitrocamphor changes corresponds to the formation of from 5 to 10 per cent of the pseudo-form in solution.

It has not been found possible to isolate pseudonitrocamphor as yet. In the case of πα'-bromonitrocamphor, however, three different crystalline forms are known. The author is of opinion that the orthorhombic modification melting at 142°, which has a specific rotatory power changing from +189° to −40° in a 3·33 per cent benzene solution, is the pseudo-form, and that the tetragonal form melting at 186°, which has a specific rotatory power changing from −50° to −40°, is the pure normal πα'-bromonitrocamphor. The third microcrystalline modification, melting at 126°, appears to be composed of the two isodynamic forms in the ratio of one part of the normal to about five of the pseudo-compound. Equilibrium is attained in solution by all the three modifications at a point corresponding to the presence of only about 4 per cent of the pseudo-compound; the fact that this form is nevertheless the one most readily obtained on crystallisation is not difficult to account for as it is much less soluble than the normal compound.

The camphornitrophenol which Cazeneuve obtained by the action of concentrated muriatic acid on nitrocamphor obviously represents a third form of isomerism, as it behaves as a saturated compound and shows phenolic properties. Its behaviour is not explained by the formula,—



proposed by Cazeneuve, since this represents it as being merely the enolic form of nitrocamphor. A change similar to that produced by hydrogen chloride occurs when benzoyl chloride acts on an alkaline solution of nitrocamphor, the product being camphornitrophenol benzoate. Cazeneuve has suggested that the formation of camphornitrophenol is due to the addition and subsequent loss of a molecular proportion of hydrogen chloride; it is possible that benzoyl chloride acts in a similar way by forming an additive compound from which hydrogen chloride is subsequently removed. The author is engaged in studying camphornitrophenol as well as its isomerides with a view of determining their inter-relationships.

*90. *Cannabinol.*" By T. B. WOOD, M.A., W. T. N. SPIVEY, M.A., and T. H. EASTERFIELD, M.A., Ph.D.

Notwithstanding the experimental evidence already adduced by the authors in favour of the homogeneity of cannabinol (*Trans.*, 1896, lxix., 539; *Proc.*, 1898, xiv., 66), further investigation has shown that the substance is a mixture.

The crystalline acetyl derivative to which the formula $C_{15}H_{18}O_2$ was assigned (*Proc.*, *loc. cit.*) is found by molecular weight determinations to possess the formula $C_{23}H_{28}O_3$, which has the same percentage composition. This conclusion is supported by the determination of the acetyl and by the examination of the other product of hydrolysis, which has the composition and molecular weight required for the formula $C_{21}H_{26}O_2$. Most of the samples of cannabinol examined have yielded about 20 per cent of the crystalline acetyl compound, together with an oily acetyl derivative containing a lower percentage of carbon.

The compound $C_{21}H_{26}O_2$ boils at 280—290° under 80 m.m. pressure. When dissolved in glacial acetic acid and treated in the cold with fuming nitric acid, it yields a bright yellow crystalline *nitro*-derivative, $C_{21}H_{23}N_3O_8$, which is more conveniently obtained by the action of nitric acid on cannabinol under similar conditions, the yield amounting to 20 per cent of the cannabinol used. This nitro-derivative melts at 160° with decomposition, has acid properties, and gives characteristic *ammonium*, *potassium*, and *silver* salts which are sparingly soluble in water, but dissolve easily in alcohol, and have the general formula $C_{21}H_{22}N_3O_8M$. The *sodium* salt is comparatively soluble and crystallises with four molecular proportions of

water. On reduction, the nitro-compound yields a corresponding base. Hot fuming nitric acid oxidises the nitro-compound to nitrocannabinolactone (oxycannabin), a mixture of acids being produced at the same time.

Amidocannabinolactone, $C_{11}H_{11}NH_2O_2$ (*Proc., loc. cit.*), has been diazotised and converted into a crystalline *iodolactone*, $C_{11}H_{11}IO_2$, which melts at 137·5° and can be sublimed. On removal of iodine from this compound by the action of sodium amalgam an oily lactone is obtained.

*91. "*An Improved Form of Gas-analysis Apparatus.*" By William A. Bone.

The author has devised an improved form of gas-analysis apparatus, suitable for all purposes where considerable accuracy in estimating small quantities of gases is required.

The apparatus consists essentially of—(1) A measuring vessel, A, made in one piece with a barometer tube, B. Both A and B are 700 m.m. long, and have the same internal and external diameters, viz., 15 and 17 m.m. respectively. B is very accurately graduated into millimetres. A and B are enclosed in a rectangular water-jacket, through which a stream of water at a constant temperature can be made to flow, and are connected by means of special steel joints and a steel tap to a movable mercury reservoir. (2) A laboratory vessel standing in a mahogany trough over mercury, into which the gases can be sent for absorption purposes. (3) An explosion vessel, similar to but rather larger than that of the Dittmar apparatus, in which all explosions are carried out.

The measuring vessel is provided with a three-way glass tap having two parallel capillary branches, one of which goes to the laboratory vessel, the other to the explosion vessel; the junctions are rendered vacuum tight by a device of steel faces and a clamp similar to that introduced by Regnault.

The moist gases are measured by bringing them to a certain constant volume in A, and then deducing their tension in terms of millimetres of mercury from the reading on the barometer, B. Since the gases in A are moist, and the "vacuum" in B is always kept saturated with water vapour, it is obvious that, provided the temperature of the water surrounding A and B remain constant throughout an analysis, none of the usual corrections for temperature, tension of water vapour, &c., need be applied to the analytical figures, as differences in readings on the barometer, under these conditions, correspond to differences in volume in the gases measured.

Discussion.

Prof. McLeod thought that too much credit was ascribed to him for the gas-analysis apparatus, which was only a modification and simplification of that devised by Sir Edward Frankland. He had done away with the centre filling tube, so that a narrower glass cylinder which could be closed by an indiarubber plug was sufficient, thus avoiding complicated metal work; he had also lengthened the barometer, and thought that the author diminished the accuracy of his apparatus by making the barometer and measuring tube of the same length. All the stopcocks were made of glass, which seemed preferable to steel, as any leakage could be more easily detected and remedied. One small part of the apparatus he did claim, and that was the suspended globular mercury reservoir, and he was gratified to see that this simple device was in use in very many forms of apparatus in which mercury is employed.

Mr. G. N. Huntly said that he had been working for some time with a slightly modified form of the Frankland apparatus, in which the black glass points of Joly were used instead of lines etched round the tube. The accuracy of this method of reading is so great that a tube of 1 inch diameter can be used without loss of precision. The author's experience with the Dittmar-Lennox pipette did not agree with his own, as experiments made with a view of testing these pipettes showed that 5 c.c. of gas, measured initially at atmospheric pressure, could be transferred backwards and forwards repeatedly without the readings on the barometer tube differing by more than 0·1 m.m., an accuracy of 1 in 7000. With careless working, transference tended, not to a loss of gas as the author suggested, but to a gain, minute air bubbles being introduced apparently from the fingers.

*92. "*Preliminary Note on the Action of Light on Acetylene.*" By William A. Bone and John Wilson.

Some time ago the authors noticed that acetylene undergoes a well-marked change on exposure to bright sunlight. Tubes of about 100 c.c. capacity, drawn out at each end and terminated by capillary glass taps, were filled at atmospheric pressure with pure acetylene prepared from copper acetylide, and dried by passing through a concentrated solution of potassium hydroxide. Some of these tubes were exposed on the roof of the laboratory throughout June and July of last year, when the weather was particularly fine. After two or three days' exposure, a faint brown deposit was observable on the inside of the bulbs. This gradually increased in extent and thickness until, at the end of a fortnight, the tubes were entirely covered with a dark brown greasy deposit. The change was evidently due to the action of sunlight, for if a portion of the tube were screened from the light no deposit was formed over the area so protected, and, further, after the tube had become coated with the opaque deposit no further action was noticeable, even after prolonged exposure. Acetylene was decomposed to a less extent when exposed in tubes during August and September, 1897, than during the previous two months. The decomposition is independent of the presence of air, because acetylene mixed with its own volume of oxygen or nitrogen was exposed to sunlight for a very long period without any appreciable change occurring.

A slight contraction in volume was observed when tubes exposed during last summer were opened over mercury. A measured quantity of the gas sent into a Hempel pipette containing a freshly prepared ammoniacal solution of cuprous chloride was quickly reduced to about 2 per cent of its original volume. The residual gas, after treatment with dilute sulphuric acid, appeared to contain a fairly dense hydrocarbon absorbed by fuming sulphuric acid, mixed possibly with a small quantity of hydrogen; no saturated hydrocarbon could be detected.

The solid deposit on the side of the tube was removed by treatment with fuming nitric acid, in which it does not dissolve to any appreciable extent. On removal of the acid by filtration, irregular yellow plates remained. The acid filtrate was carefully tested for the presence of nitro-derivatives of benzene and naphthalene, but without success. The yellow plates were insoluble in hot benzene, and could be heated at 270° without melting or undergoing any change; they apparently consisted of a very dense hydrocarbon or hydrocarbons.

The authors are working this summer on larger volumes of acetylene, and hope eventually to determine the nature of the products obtained.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, June 24th, 1898.

Mr. Walter Baily in the Chair.

Prof. Carus-Wilson exhibited an apparatus to illustrate the action of two electric-motors coupled in such a way as to admit of their rotating at different speeds. The two shafts are placed in line, and each is fitted with a bevel-wheel gearing into an intermediate wheel. The axis of the intermediate wheel is at right angles to the line of the motor-shafts, and is free to rotate in a plane at right-angles to that line. The motors can be made to rotate

at different speeds by altering the strength of the magnets of either or both. The motion of the intermediate wheel depends upon the difference of the two speeds, or upon their mean, according to their relative directions of rotation. A simple graphic construction enables the action to be pre-determined for any given load on the intermediate wheel. Calling the two motors A and B, and the intermediate wheel C, lines can be drawn on a base of current, to represent the speeds and the torques for each motor. If the motions of A and B are in the same direction, the load or torque is the same on each, and of similar sign. Hence, as the load on the wheel C is increased, the speeds of A and B tend to become equal (if A had been running faster than B); and for a certain load on C the speeds of A and B will be equal. If the load on C is further increased, B will run faster than A. Also, there will be a certain value for the load on C at which the motion of A will reverse. A further increase of the load on C will bring C to rest, A and B then rotating at equal speeds in opposite directions. When the load on C is nothing, let the motors rotate in opposite directions, A running faster than B. The motion of C now depends upon the difference of speeds of A and B. When a load is put on C, the motion of A is retarded, while that of B is assisted; hence B takes less current, and A takes more. The torques on the two motors, due to the load on C, are now of equal amount, but of opposite sign. As the load on C is increased, the speed of A is reduced, and that of B increased, until the two are equal and C comes to rest. B is now acting as a generator, and sending current into A. If the load on C is simply that due to friction, the process cannot be carried further. But if the load on C is reversed, the speed of B becomes greater than that of A, and the motion of C is reversed. In the steering gear designed by the Union Electricitäts Gesellschaft, the intermediate wheel is made to actuate a rudder, by differential action. The motion is reversed by making the speed of one motor greater or less than that of the other.

Mr. Quick then exhibited Weedon's apparatus for the measurement of the expansion of solids. This method is claimed to be independent of knowledge of optics on the part of the student. The expansion is read directly by means of a pair of micrometers. Precautions are taken to prevent errors due to radiation.

Mr. Lehfeldt asked what precautions were taken to prevent the movement of the micrometer supports.

Mr. Stansfield described a form of apparatus in use at Chelsea Polytechnic; it was a simple contrivance, in which changes of length were measured by a micrometer.

Mr. Quick, replying, thought the instrument referred to by Mr. Stansfield pre-supposed a knowledge of optics.

Mr. Lehfeldt then read a paper, by Dr. Donnan, on the "*Theory of the Hall Effect in a Binary Electrolyte.*"

In 1883 Roiti investigated the subject of a possible Hall effect in electrolytic solutions. He failed to obtain any positive result. Recently the question has been examined by Bagard, who noticed certain effects in aqueous solutions of zincic and cupric sulphates. Meanwhile negative results have been observed by Florio. The author therefore discusses what effect might be expected by theory, on somewhat the same lines as those of Van Everdingen, Jr., taking a more general case. So far as the present discussion goes, the author's theory is wholly in favour of the negative results of Roiti and Florio. It would appear that Bagard measured a phenomenon not contemplated by the theory as stated in the present treatment. Van Everdingen originally supported the positive results of Bagard; but his work, unfortunately, was rendered incorrect by the accidental omission of a numerical factor. He has since discovered the slip in his calculations, and now agrees with the author's conclusions.

The Chairman proposed votes of thanks to the authors, and the meeting adjourned until October, this being the last of the Session.

NOTICES OF BOOKS.

The Kinetic Imagining of Gases. (An Open Letter). By Stephen H. Emmens. New York.

We are in receipt of a remarkable pseudo-scientific pamphlet bearing the above title. Considering its shortness it contains a wonderful collection of errors and fallacies, and shows considerable internal evidence that the author has either had no scientific training or has not known how to profit by it.

The subject of the pamphlet is a crude attack on the Kinetic Theory of Gases, and on the people who believe in it; but we are of opinion that the theory in question is sufficiently firmly established to withstand more formidable assaults than this.

The author, after appealing to the scientific public for careful consideration, opens by describing half an experiment, and asking them to draw a whole conclusion from it. This is an error which, we trust, none but novices, and but few of them, will fall into.

In the next place, he challenges the world to adduce a single observed fact in proof of the Kinetic Theory of Gases. This is a well-known schoolboy method of arguing. Might we gently hint, however, to the author that, since he is attacking an accepted theory, the onus of proof lies with him?

His next remark is even wilder, for he quotes the cathode rays as not behaving according to theory. May we ask which theory? There are several provisional theories to choose from, though neither is generally accepted.

He then goes on to invite all who are desirous of seeing error replaced by truth—a laudable desire—to aid in collecting natural facts showing the Kinetic Theory of Gases to be but a vain imagining. We need hardly point out that any one who enters on a research with a preconceived idea of what the result is to be, is likely to arrive at an untrustworthy conclusion, and must not be surprised if a critical public declines to accept it at its face value.

He concludes by drawing attention to the bad reception which Charles Darwin's theory of the Origin of Species met with when first it was propounded, and infers that every new theory which is badly received by scientific men is, *ipse facto*, true. The fallacy involved is apparent.

We would point out to the author that the first requisite of a scientific man is an open mind; the second is the skill to perform careful and accurate experiments and record them correctly; and the third is the ability to draw correct conclusions from them: the pamphlet under review offers no evidence that he is possessed of any one of them.

OBITUARY.

Dr. A. D. van RIEMSDIJK.

In the twenty-eighth Annual Report of the Deputy Master of the Mint, just issued, we find a fitting tribute to the memory of the late Dr. van Riemsdijk, Director of the Utrecht Mint, which occurred on the 26th of April last, when Holland lost an eminent chemist. He was one of a small band of scientific workers who, some forty years ago, influenced by the late Prof. Stas, conducted elaborate investigations with a view to improve the operations of coinage. The results of his own researches not only contributed to accuracy in assaying, but have been of material service in connection with certain chemical operations which are conducted in Mints. He was an

excellent chemist, and always ready to assist his *confrères* with his advice. These few words are offered in sincere appreciation of the value of his labours.

CORRESPONDENCE.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—If Mr. Droop Richmond is the gentleman who, six years ago, wrote an elaborate paper to announce the discovery of a new element—of which nothing has since been heard,—he is certainly a high authority upon the new gases. But he has evidently not cured himself of the precipitancy of judgment he then displayed, otherwise he would not have committed himself to the groundless and utterly erroneous assumption that I had to wait for Rayleigh and Ramsay to learn about the classical experiment of Cavendish. I was acquainted with that before I left school.

It is satisfactory to find that this eminent authority does not upset or even seriously assail a single proposition advanced in the letter you did me the honour to publish. On the contrary, he concedes my main contention when he says that I "might wait a year or so, and give Professor Ramsay time to do the work he has mapped out for himself." The whole point is, that he has not taken the time everyone was willing to give him, but has hastily announced results—some of which are already proved to be erroneous, and none of which have yet been made out with scientific precision. The Cavendish residue was declared to be argon; and argon, *pace* Mr. Richmond, was loudly and even angrily declared to be an element, notwithstanding the warnings of the judicious. That residue is now declared to contain argon, krypton, neon, and metargon; but not one of the four has been any better made out than the famous Masrium that Mr. Richmond wrote of. There is nothing to show for them except spectral lines, some of which were noted years ago by Liveing and Dewar, and some by Moissan and Deslandres. Not one of the four thought of claiming the discovery of a new element, though all suspected its existence. Their procedure contrasts sharply with that of Professor Ramsay.

I am happy to be able to agree with Mr. Richmond on one point—that the real discoverer of argon is Lord Rayleigh. What he felt "as a physicist" I do not know, but I shrewdly suspect that he felt as a man more than than he has told the public. Whatever he felt as a physicist, he did not "associate himself with a chemist." It was the other way about; the chemist compelled Lord Rayleigh to accept a wholly unsought association with him. Lord Rayleigh, as he has told us himself, was directed by Professor Dewar to the experiment of Cavendish as the solution of his difficulty about the discrepant weights of nitrogen from different sources. But for that fortunate circumstance he would have lost more than the half share of the fruit of his admirably solid and accurate work.

For the direction subsequently given to the work, Lord Rayleigh—as a physicist, and not a chemist—is responsible only indirectly and under compulsion.

I have the more pleasure in thus fully correcting my "inadvertence," which I regret, Sir, to see somewhat illogically charged against you, because Professor Ramsay, with his usual scrupulous fairness, has hastened to point out that both Lord Rayleigh and Mr. Travers have a large share in what has been done.—I am, &c.,

Suum Cuique.

London, June 27, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 18, May 2, 1898.

Researches on the State in which Silicon and Chromium occur in Siderurgical Products.—A. Carnot and M. Goutal.—The authors have already found that silicon and chromium combine with iron, manganese, and carbon; but the complexity of these compounds has necessitated further researches, which are here described. They also observed the existence of other compounds of silicon besides the silicide of iron, and these are now given with greater accuracy. Amongst other things, they conclude, from a number of experiments, that these siderurgic products contain two combinations of iron and silicon corresponding to the formulæ SiFe and $SiFe_2$; further, when sufficiently rich in manganese they may contain a silicide of the form $SiMn_3$. In the case of ferrochromes, there should be three molecules of carbide of chromium with one molecule of carbide of iron.

Dimethylamido-diethylamido-orthobenzoyl and Orthobenzylbenzoic acids, and some of their Derivatives.—A. Haller and A. Guyot.—The authors state that the memoir recently published by M. Limpricht (*Liebig's Annalen*, ccc., p. 228) contains results already published by them (*Comptes Rendus*, cix.; *Ber. der Deut. Chem. Ges.*, xxviii.; *Bull. Soc. Chim.*, [3], vols. xv. and xvii., &c.), as well as other results since obtained. The paper is partly controversial, but a number of new compounds are described.

On the Radiations emitted by Thorium and its Compounds.—G. C. Schmidt.—The author points out that the paper recently read at the Academy by Mdlle. Curie on this subject was anticipated by his communication to the Physical Society of Berlin on Feb. 4, 1898. He now gives the values he obtained with citrate of uranium, nitrate of uranium, oxide of thorium, sulphate of thorium, and nitrate of thorium.

On Iodide of Glucinum.—P. Lebeau.—Already inserted in full.

New Reaction of Tertiary Alcohols and their Ethers.—G. Denigès.—To apply the method already described by the author (*Comptes Rendus*, cxxvi., p. 1145) to the tertiary alcohols, it is necessary to heat a few c.c. of the alcohol in question with a few c.c. of the mercuric reagent used for the ethenic carbides, viz., HgO, 50 grms.; H_2SO_4, 200 grms.; and water, 1000 grms. A more or less yellow precipitate is at once formed; it sometimes has a reddish tinge, varying according to the alcohol used. The present paper is confined principally to the best known ones, and those easiest to obtain; that is, trimethyl carbinol, and ethyl dimethyl carbinol, so as to show the identity of the derivatives obtained with these alcohols and the corresponding ethenic carbides. The ethers of the tertiary alcohols also react with mercuric sulphate when gently warmed, furnishing yellow mercuric compounds. The action is very distinct with the tertiary nitrite of amyl used in medicine.

Action of Alkalis on Ouabaine.—M. Arnaud.—The alkalis do not hydrolyse ouabaine even when boiled, but give rise to a dehydrated derivative formed without splitting up and without the production of reducing sugar. The body formed is a monobasic acid, which decomposes the alkaline carbonates or the alkaline earths, and reddens blue litmus. Ouabaic acid, as it is called, is a yellowish white amorphous body, resembling gum; it is very soluble in water, slightly so in alcohol, but insoluble in ether. It melts at about 235°, decomposing and giving off a gas smelling of caramel. Its formula, deduced from the ana-

lysis of its salts, is $C_{30}H_{48}O_{13}$. The author proceeds to describe a number of its compounds, such as the ouabates of sodium, strontium, barium, &c.

Action of Bromine in the presence of Bromide of Aluminium on some Phenols.—F. Bodroux.—The author has applied the method of MM. Blumlein and Flessa to the bromidation of a number of phenols of the benzenic series by treating the phenol with an excess of bromine containing 1 per cent of aluminium in solution. After six hours the mixture is evaporated and treated with an appropriate solvent. The results obtained from nine different phenols are described at length. The action of bromine on the nitrophenols was found to be less strong in the presence of bromide of aluminium than when this latter body was not present.

The Monophosphoric Ethers.—J. Cavalier.—A criticism on a note recently presented to the Academy by M. Belugou (*C. R.*, April 18, 1898). The authors do not agree on all points.

Berichte der Deutschen Chemischen Gesellschaft.
December 13, 1897.

Reciprocal Transformation of Optical Isomers one in the other.—P. Walden and O. Lutz.—The authors have noticed the remarkable fact that when a solution of ammonia in methylic alcohol is made to act on a solution of left-handed chlorosuccinic acid, or left-handed bromosuccinic acid in the same solvent, and the rotatory power be followed with the polarimeter, it will be seen that the deviation gradually becomes less and less, disappears, and then becomes levogyre. It remains constant at the end of ten or twelve hours.

Regularity of the Increase of the Boiling-points of the Isomers of the Fatty Series.—N. Menschutkin.—The variations of the boiling-points of the isomeric alcohols, and in general the saturated compounds of the fatty series, depend—(1) On the length of the principal hydrocarbon chain; (2) on the number of lateral chains and their manner of attachment to the principal chain; (3) on the distance of the point of attachment of these chains from the functional grouping. As examples, the amylic and hexylic alcohols are cited.

Contributions to the Study of the Hydrocarbon Chains of the Fatty Series.—N. Menschutkin.—The author has studied the speed of the reaction of the fatty amines with bromide of allyl at 100°, using the following proportions:—Amine, 2 mols.; bromide of allyl, 1 mol.; benzene, 15 parts. He finds that the value of K decreases rapidly when passing from a lower to a higher homologue if the atoms are simply attached and the chain remains open. Whatever the constitution of the amine, the speed of the reaction is always greater with bromide of methyl than with bromide of allyl. With an amine having a secondary chain, the speed of the reaction varies little when the longest of the hydrocarbon branches is lengthened.

Stereo-isomeric Chlorobromosuccinic Acids.—P. Walden.—A racemic chlorobromosuccinic acid was prepared by heating 10 grms. of chlorofumaric acid with 35 grms. of a solution of HBr gas in acetic acid first to 125° and then to 140° in a closed glass vessel. On cooling, the product crystallises out in plates; it decomposes at 235—237°. Distilled with an excess of P_2O_5 it is transformed into chloromalic anhydride, boiling at 205°.

Some Derivatives of Prozane.—J. Thiele and W. Osborne.—The authors give the name "prozane" to the hypothetical compound $NH_2.NH.NH_2$. By acting on nitrate of diazoguanidine with CNK, the cyanide $CN.N = N.NH.C\leq^{NH_2}_{NH}$ is obtained in difficultly soluble yellow needles. Mineral acids transform it into formamido-diazo-amino-formamidine, crystallising also in yellow needles, and detonating at 140°. The careful reduction of the formamide gives the compound $NH_2.CO.NH.NH.NH.C\leq^{NH}_{NH_2}$, which decomposes spontaneously at a low temperature.

Some Organo-metallic Derivatives.—A. Michaelis.—Several series of organo-metallic and organo-metalloidic compounds have been prepared by acting on certain aromatic compounds with the chlorides of selenium, tellurium, bismuth, &c.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Decolourising Oils.—Would any of your kind readers give me the names of materials used in decolourising oils, either with a hot or cold process, such oils to be used for lubricating purposes and to have no acid reaction when finished.—H. Matthews.

THE
ARRANGEMENT OF ATOMS IN SPACE.
By J. H. VAN 'T HOFF.
Second, Revised, and Enlarged Edition.
With a Preface by Johannes Wislicenus, Professor of Chemistry at the University of Leipzig;
and an Appendix, 'Stereochemistry among Inorganic Substances,' by Alfred Werner, Professor of Chemistry at the University of Zurich.
Translated and Edited by ARNOLD EILOART.
London, New York, and Bombay:
LONGMANS, GREEN, & CO.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2015.

THE ACTION OF DI-ISOCYANATES UPON AMIDO-COMPOUNDS.

By H. LLOYD SNAPE, D.Sc., Ph.D.

In a paper published in the Chemical News (lxxiii., p. 37) I described the behaviour of diphenylene di-isocyanate towards ammonia and aniline. I have since submitted the same cyanate to the action of phenyl-hydrazine. As far as I can discover, the reaction of phenyl-hydrazine upon a di-isocyanate has not been examined; but if the former acted similarly to ammonia and aniline, two molecules of the base would combine directly with one molecule of the di-cyanate.

$$\begin{matrix} C_6H_4\cdot NCO \\ | \\ C_6H_4\cdot NCO \end{matrix} + 2C_6H_5\cdot NH\cdot NH_2 = \begin{matrix} C_6H_4\cdot NH\cdot CO\cdot NH\cdot NH\cdot C_6H_5 \\ | \\ C_6H_4\cdot NH\cdot CO\cdot NH\cdot NH\cdot C_6H_5. \end{matrix}$$

Combination was actually found to occur in accordance with this equation.

Diphenylene di-Phenylsemicarbazide.

Diphenylene di-isocyanate was dissolved in absolute ether and mixed with an ethereal solution of phenyl-hydrazine, the latter being taken in excess of the quantity theoretically required. A white powder immediately separated. This was extracted with boiling alcohol. The residue did not melt at 300°, and was insoluble in ether, chloroform, carbon tetrachloride, benzene, and petroleum-ether. As no suitable solvent was discovered for this compound, it was at once analysed, after drying *in vacuo* over sulphuric acid, and was found to have the constitution anticipated.

0·1899 gave 0·4816 CO_2 and 0·0953 H_2O. C = 69·16; H = 5·57.
0·0999 gave 16 c.c. moist N at 17° and 773·7 m.m. N = 18·87.
Required for $C_{26}H_{24}N_6O_2$, C = 69·03; H = 5·31; N = 18·58 per cent.

On the addition of a solution of copper sulphate to an alcoholic solution of the above substance a chocolate-brown colouration was obtained, which changed to green on the addition of ammonia.

1-2-4 *Toluylene di-Phenylsemicarbazide*, $CH_3\cdot C_6H_3(NH\cdot CO\cdot NH\cdot NH\cdot C_6H_5)_2$.

This compound was produced by a precisely similar reaction, substituting the toluylene for the diphenylene di-isocyanate. The product was in this case, however, difficultly soluble in alcohol, and was re-crystallised from the solvent. The crystals thus obtained decomposed, and rose in a capillary tube at 203°. They were insoluble in ether, chloroform, benzene, petroleum ether, and carbon disulphide. A few drops of copper sulphate solution, when added to an alcoholic solution of the substance, gave a wine-red colouration, which changed to green on the addition of ammonia.

0·204 gave 0·4803 CO_2 and 0·1066 H_2O. C = 64·21; H = 5·80.
0·1228 gave 21·9 c.c. moist N at 14° and 776·9 m.m. N = 21·45.
Required for $C_{21}H_{22}N_6O_2$, C = 64·62; H = 5·64; N = 21·54 per cent.

1-2-4 *Diphenyl-toluylene-diurea*, $CH_3\cdot C_6H_3(NH\cdot CO\cdot NH\cdot C_6H_5)_2$.

When an ethereal solution of toluylene di-isocyanate was added to aniline also dissolved in absolute ether, combination took place immediately, and was attended by evolution of heat. By re-crystallisation from alcohol, microscopic needles were obtained which melted at 261° with accompanying decomposition, a gas being evolved which had the odour of phenyl cyanate. The crystals were only slightly soluble in methyl, ethyl, and amyl alcohol, and were insoluble in ether, chloroform, carbon tetrachloride, benzene, toluene, petroleum ether, and carbon disulphide, but dissolved readily in concentrated sulphuric acid.

0·1936 gave 0·4963 CO_2 and 0·0999 H_2O. C = 69·91; H = 5·73.
0·2231 gave 0·5732 CO_2 and 0·1132 H_2O. C = 70·07; H = 5·64.
0·1939 gave 25·9 c.c. moist N at 19° and 767·8 m.m. N = 15·51.
Required for $C_{21}H_{20}N_4O_2$, C = 70·00; H = 5·56; N = 15·55 per cent.

Kuehn described (*Berichte d. D. Chem. Gesell.*, xviii., 1477) a compound having the above formula, which he obtained by the action of phenyl isocyanate upon meta-toluylene-diamine. It was to be anticipated that this would be identical with the compound prepared as above. He states, however, that the substance was insoluble in all ordinary solvents save aniline, by which it was decomposed, and that its melting-point was above 300°. On repeating Kuehn's experiment, a fine white amorphous powder was obtained, which did not melt even at 325°; bnt, after boiling with alcohol, the residue and also the crystals from the alcoholic solution melted at 261° with decomposition, and appeared to be in every respect identical with that obtained from the toluylene di-cyanate. The compound of higher melting-point (as prepared by Kuehn's method) was also successively extracted with ether, chloroform, petroleum ether, benzene, and carbon disulphide. A very small quantity was dissolved out by the first two solvents named, and again the residue melted at about 260°.

1-2-4 *Toluylene di-urea*, $CH_3\cdot C_6H_3(NH\cdot CO\cdot NH_2)_2$.

A stream of dry ammonia gas was led into a solution of meta-toluylene di-isocyanate in absolute ether. The white precipitate yielded, by crystallisation from water, tufts of minute crystals which melted and rose in a capillary tube at ca. 252°. The crystals were only sparingly soluble in alcohol, and were insoluble in ether, chloroform, benzene, petroleum-ether, and carbon disulphide.

0·1856 gave 41·6 c.c. moist N at 14·3° and 775·5 m.m. N = 26·87.
Required for $C_9H_{12}N_4O_2$, N = 26·92 per cent.

Strauss described (*Liebig's Annalen*, cxlviii., 159) a substance which he named toluylene di-urea. This he obtained by the action of potassium cyanate upon the sulphate of a base which he terms "toluylen-diamin." The only such compound then known was the 1-2-4 isomeride; and hence it was to be anticipated that the urea obtained by him would be identical with that described above. He stated that the melting-point of the substance prepared by him was 220°. As the melting-point was about 30° lower than that obtained by me, I repeated Strauss's experiment. The sulphate was prepared from the same sample of meta-toluylene-diamine (m.pt. 99°, b.pt. 282—283°, obtained from Kahlbaum) as that I had used in the preparation of the di-isocyanate. The product, which separated on standing, was re-crystallised first from water and then from alcohol. The crystals thus obtained melted with decomposition at ca. 252°, and that they consisted of the di-urea was shown by the following analytical results:—

0·195 gave 0·3689 CO_2 and 0·1025 H_2O. C = 51·59; H = 5·84.
0·1006 gave 22·5 c.c. moist N at 10° and 763 m.m. N = 26·88.
Required for $C_9H_{12}N_4O_2$, C = 51·92; H = 5·77; N = 26·92 per cent.

Lussy records (*Berichte d. D. Chem. Gesell.*, viii., 291) that he obtained the same substance as that prepared by Strauss, by the action of ammonia on toluylene di-isocyanate. The only difference between Lussy's experiment and my own, as far as may be determined from the literature, is that he prepared his di-isocyanate by the action of phosphoric anhydride upon the corresponding urethane, whereas I obtained mine direct from the toluylene diamine by the action of phosgene, by the method described by me (*Journ. Chem. Soc.*, xlix., 255). As, however, the melting-points of both the cyanate and the urethane prepared by Lussy and myself are in agreement, this does not account for the large difference in the melting-points of the di-urea.

University College of Wales, Aberystwith.

SEPARATIONS WITH ALKALINE CHROMATES.

By HARRY BREARLEY.

Those reactions which, by the formation of basic chromates, interfere with the separation of aluminium, iron, manganese, chromium, &c., from chromic acid, may be made the basis of a number of useful separations. It is possible, also, to use the chromates to suggest an explanation, by analogy, of some obscure points in the basic acetate separation of iron.

The Separation of Iron and Aluminium.

Two or three times during the past year there has been occasion to notice, when an acetate separation of iron was made in the presence of aluminium and an alkaline chromate, that a considerable portion of alumina was to be found in the filtrate. A comparison of the behaviour of ferric and aluminic solutions on adding K_2CrO_4 clearly explains the result; for while ferric salts are precipitated more readily in hot than in cold solutions, the aluminic salts are precipitated less readily in the hot solution, and moreover the latter, in any case, less readily forms basic chromates than the former.

Turning to "neutralised" solutions,—that is, those holding the full amount of dissolved hydrate,—we find that half a grm. of iron may be readily precipitated by 10 c.c. potassium chromate (12½ grs. per litre), but that half a grm. of Al in a like state needs 50 c.c. K_2CrO_4 to form a partial precipitate. More strikingly still, the ferric precipitate is insoluble, in hot solution, in presence of free acetic acid, while the Al precipitate is *very* easily soluble, so that, although half a grm. of iron is precipitated as before with 10 c.c. K_2CrO_4 when 10 c.c. of acetic acid (33 per cent) is present, half a grm. of Al with its 50 c.c. K_2CrO_4 does not show the faintest trace of a precipitate when the same amount of acetic acid is present.

The obvious inference is that one has only to neutralise the mixture (Al+Fe), heat to boiling, add potassium chromate, and straightway effect an easy separation of iron and aluminium. Unfortunately such an inference may not be supported experimentally. The difficulty consists of the iron refusing to be precipitated until many times more K_2CrO_4 has been added than would be needed if no aluminium was present, and in ultimately carrying down with it so great a proportion of Al as spoils a quantitative separation.

A set of circumstances almost parallel can be associated with the behaviour of a "neutralised" mixture of Fe and Al salts to alkaline acetates. This latter case, however, is of such frequent occurrence in the steel works laboratory that one has ceased altogether to be astonished at it. Even the text-books special to steel analysis, after drawing attention to the solubility of the hydrates and acetates of alumina in free acetic acid, explain the absence of this element from the filtrates by the not too satisfactory remark that "the chromium and aluminium are completely carried down with the iron precipitate."

Inured as one may be to the above phenomenon of acetate separations, the behaviour of the mixed solutions of Fe and Al to an alkaline chromate has all the novelty of a most unexpected result, and one is prompted by disappointment to question the right of solutions to behave so.

The cause of the failure with chromate may go some way towards explaining the failure with acetate, and the liberty of chronicling a failure may be further justified by some peculiarities which were brought to light in attempting to find experimentally the cause of failure.

Soda carbonate had been used for "neutralising" the metallic solutions. This would precipitate the iron as hydrate and the alumina as basic carbonate; for the sake of brevity, however, we may speak of the united precipitates as hydrates.

Solubility of Ferric Hydrate and Basic Al Carbonate in Ferric Chloride and Aluminic Chloride.

According to "Comey's Dictionary," p. 6, precipitated aluminium hydroxide is insoluble in ferric chloride. Gmelin ("Handbook," v., 277) states the contrary to be the case. I find that 1/10th of a grm. of iron as ferric chloride readily dissolves a quarter of a grm. of Al which has been freshly precipitated from a solution of Al_2Cl_6, by adding an equivalent amount of soda carbonate. The solution becomes dark mahogany-coloured, just as when ferric hydrate is being dissolved. In 1/10th of a grm. of Al, in a similar way, one may dissolve precipitated ferric hydrate, but here the reaction is much slower; however, more than a quarter of a grm. is dissolved with only a faint opalescence; and when half a grm. of iron, as ferric hydrate, is added, only a very small precipitate remains undissolved on standing.

A mixture of ferric and aluminic chloride, on being neutralised, offers every advantage for this mutual solubility to display itself. This being done, the added chromate might be assumed to precipitate the remnant of ferric chloride along with the dissolved ferric and aluminic hydrates. This would account for so much of the Al being carried down with the iron. If we assume that the chloride of aluminium, having dissolved large amounts of $Fe_2(HO)_6$, must be itself decomposed before the iron can be completely separated, and so account for the larger amounts of K_2CrO_4 found to be necessary, we are unable to account for so much of the alumina as does always exist in the filtrate. I am inclined to think that the solution of ferric hydrate in the Al_2Cl_6 does not take place, owing to the comparative slowness of the reaction, to any great extent; and for the rest I think it is more satisfactory, and not more difficult, to assume that the properties of the ferric chloride are greatly modified by the dissolved basic carbonate of alumina which it has dissolved, one result of which is that it behaves to the K_2CrO_4 rather as an aluminic than a ferric salt.*

The following experiments indicate a reaction between the neutralised solutions of Al and Fe, whose significance in this connection can be well understood, but whose nature has not yet been made out. In each test ½ grm. Fe and ½ grm. Al was used, volume of solution about 300 c.c.:—

(1) Solution completely neutralised: added 20 c.c. K_2CrO_4, no precipitate; 10 c.c. K_2CrO_4 more, precipitate

* If the ferric chloride, on "neutralisation," dissolved the combined precipitates in more than equivalent portions, and so preserved itself more as undecomposed chloride holding dissolved hydrates, it would necessarily need larger amounts of K_2CrO_4 to decompose it, but not nearly such large amounts as are found to be necessary.

on continued boiling; less than one-fourth of the Al was found in the filtrate.

(2) Repeated (1) and continued the boiling for some time; then added 10 c.c. of acetic acid, with intent to redissolve the precipitated $Al_2O_3,yCrO_3$, which is so easily soluble in acetic acid; but the total precipitate dissolved, although the ferric compound is quite insoluble alone. If the acetic acid be added before the chromate, it is necessary to add about 70 c.c. of the latter, and then the filtrate contains also considerable iron.

(3) Neutralised the Al_2Cl_6 and Fe_2Cl_6 separately in hot solutions, then cooled and mixed them in separate portions. A precipitate is formed, and this the more readily as the proportion of aluminium is greater. The precipitates were collected on a filter, and after the mother-liquor was removed they were washed with cold water. *They dissolved* to a clear dark reddish liquid. Hot water very readily dissolves the precipitates, and gives a perfectly clear solution, very much like a "neutralised" solution of ferric chloride.

(4) "Neutralised" the solutions separately as in (3), and together as in (1), in each case using the same amounts of soda carbonate. The latter remained clear on standing or heating, but on mixing the separately neutralised solutions a precipitate was formed. The filtrate was perfectly clear and colourless, and contained nearly the whole of the aluminium.*

(5) One-tenth of a grm. iron, as ferric chloride, in which is dissolved ¼ grm. Al precipitated from its chloride solution with soda carbonate. Raised to boiling; needs 40 c.c. of the K_2CrO_4 to form a precipitate.

The foregoing experiments show conclusively, I think, that no complete separation of iron and aluminium can be made on "neutralised" solutions. The very intimate association of the two metals, under such conditions, suggest that no such separation will ever be effected.

Separation of Iron and Aluminium in Normal Solutions.

When only the free acid of a solution of iron and aluminium salts has been neutralised (without forming dissolved hydrates) the foregoing considerations do not apply. Such a state may be attained with sufficient accuracy by noting the change from yellow to red which characterises the solution of ferric hydrate in its chloride.

If it were possible to precipitate the whole of the iron when it exists as ferric chloride, then our object might easily be attained, but unfortunately—even from pure ferric chloride solutions—the iron is not completely precipitated, nor does increasing the potassium chromate noticeably better the precipitation. And, again, the precipitate is somewhat soluble in the cold mother-liquor, so that filtrations must be preserved as hot as possible.

This separation was tested on a mixture of half a grm. each of iron and aluminium. The iron was precipitated as just explained with K_2CrO_4; the filtrate was evaporated and treated with caustic soda (from Na), the small quantity of iron filtered off, and the iron precipitated as phosphate.† The precipitate was washed until the washing showed no turbidity with silver nitrate. The aluminium recovered, calculated from the ignited $AlPO_4$, was 0·5030 grm., which is less than 1 per cent from the amount added.

Separation of Iron and Chromium.

This separation cannot be completely effected in "neutralised" solutions, for the reasons previously stated in connection with aluminium.

Separation of Iron and Nickel.

Generally potassium chromate would seem to be a most excellent reagent in the same office as alkaline acetates for separating iron from various elements. There is no occasion whatever to go back on the strong recommendation of the acetate separation of iron and nickel which has been previously made; at the same time it is desirable to acknowledge the service of a reagent which can be used in much larger excesses without fear of ill results, and moreover which can be used where the acetate separation of iron and nickel begins to break down, viz., in the presence of considerable amounts (10 per cent or more) of aluminium.

Nickel can form a number of basic chromates just as iron can, but the separate compounds behave very differently under simple and easily arranged circumstances. The iron compound is readily formed in heated solutions, and is practically insoluble in dilute solutions of acetic acid. On the other hand, the formation of the nickel compound is much less readily accelerated by heating, and is *very readily* soluble in dilute acetic acid. The process is based on these facts, but, as it differs from the usual acetate separation only in the substitution of a chromate for an acetate, it needs no further description.

One grm. of iron (neutralised solution) is abundantly precipitated by 10 c.c. K_2CrO_4 (12½ grs. per litre), and the behaviour of an excess of the precipitant on an accompanying 0·1 grm. of nickel is as follows:—

10	30	50 c.c. chromate added,
0·1000	0·0998	0·0918 grs. Ni recovered,

which are better separations than proportional excesses of acetate would give even in presence of 1 per cent acetic acid. When the chromate separations are made in a 1 per cent acetic acid solution, the range of accuracy is enormously increased. The following are examples, using the previous amounts of iron and nickel:—

30	50	70 c.c. chromate used.
0·1004	0·1000	0·1000 grs. nickel recovered.

The $Fe_2(HO)_6$ liberated by the decomposed ferric chloride can react with K_2CrO_4 to form basic chromates, and hence the larger excess of the precipitant there is, the less basic these chromates are, so that the colour of the filtrate is not proportional to the excess of K_2CrO_4 used. When ample chromate is added the filtrate may be hardly coloured. In some ways the presence of K_2CrO_4 in the filtrate may be an advantage. For instance, in the cyanometric estimation of the nickel it readily indicates the neutrality of the solution. Even highly coloured filtrates have not been found to be harmful.

In preparing for the cyanometric estimation of the separated nickel, it is necessary, in presence of chromic acid, to proceed in a certain order. First add the ammonium sulphate (for the purpose of heightening the AgI turbidity, &c.), and then make alkaline with ammonia. The reason for this is that the ammonia sulphate prevents the formation, in an alkaline solution, of a basic nickel chromate (a brown precipitate which might be mistaken for ferric hydroxide), which does not so readily combine with the cyanide. If the reverse order is followed, the added ammonia sulphate does not easily dissolve this precipitate.

The acetate separation of iron from nickel in presence of aluminium was incomplete, because a greatly increased amount of acetate was needed under these conditions. In a like manner, an increased amount of chromate is necessary, but the increase is quite covered by the latitude which can safely be allowed when using the latter reagent.

The nickel is accompanied by part of the aluminium. As our test analyses contained known amounts of nickel, we performed the titration by adding a slight excess of cyanide, fractionally filtering off the alumina, and completing the reaction on the aliquot filtrate. Such results were always low. To make an accurate estimation it is necessary to keep the alumina in solution by adding (not a needlessly large amount) tartaric acid; or if the amount of Ni is approximately known, by adding a small excess of cyanide to the faintly acid or neutral solution, and

* Judging from the bulk precipitated by ammonia when compared with a standard.

† This procedure completely effects the separation of the alumina from the chromic acid (CHEM. NEWS, lxxvii., 179).

then making alkaline, filtering off Al_2O_3, &c. This point will be more fully dealt with in a later paper on cyanometric estimations.

The Separation of Iron and Copper.

The most favourable separation of these elements with acetate were 1 or 2 per cent too low. The Schwarzenberg separation even, which is not easy to perform well, did not give quite accurate results. With chromate the separation is accurate with a wider range of the precipitant than the corresponding nickel separation is: thus 50 c.c. K_2CrO_4, used in the previous—non-acetic nickel-iron—separation, separated only 91·8 per cent of the added nickel; in a like copper separation 97·0 per cent was separated. Other results are:—

10	30 c.c. chromate used.
0·0998	0·1003 grs. Cu recovered.

The chromate compound of copper is also *very* soluble in dilute acetic acid, and a greatly increased range of accuracy may fairly be expected to attend its use in case any circumstance should require very large excesses to be used.

In January of this year, when the suitability of potassium chromate for the copper-iron separation was first suggested, our Mr. Jervis made a number of tests which fully illustrated the accuracy of the process. The separated copper may be easily estimated by the soda cyanide process (Chem. News, lxxvi., 189 and 291).

It is anticipated that other separations may be made. The accuracy of the preceding separations, and the wide differences under which it may be maintained, are points of some value where technical analyses are performed by operators not too skilled.

Totley, near Sheffield.

RECENT EXPERIMENTS ON CERTAIN OF THE CHEMICAL ELEMENTS IN RELATION TO HEAT.*

By Professor W. A. TILDEN, D.Sc. F.R.S.

The discovery that different substances have different capacities for heat is usually attributed to Irvine, but there can be no doubt that Black, Crawford, and others contributed to the establishment of the idea. The fact that equal weights of different substances, in cooling down through the same number of degrees, give out different amounts of heat, may be illustrated by the well-known experiment, in which a cake of wax is penetrated with different degrees of rapidity by balls of different metals heated to the same temperature. But, for the quantitative estimation of the amounts of heat thus taken up and given out again—that is, the *specific heats*—the physicist must resort to other forms of experiment, each of which presents difficulties of its own. Broadly speaking, three principal methods have been used in the past for this purpose. The first is based upon the observation of the exact change of temperature produced in a known mass of water, by mixing with it a known weight of the substance previously, at a definite temperature above or below that of the water. The second consists in determining the quantity of ice melted, when the heated body is brought into contact with it in such a way that no heat from any other source can reach the ice. And the third method consists in observing the rate at which the temperature of the heated body falls through a definite range of degrees, when suspended in a vacuous space, as compared with the rate of cooling of another body taken as the standard.

* A Lecture delivered at the Royal Institution of Great Britain, Friday, May 13th, 1898.

The process of intermixture with water was used by the earlier experimenters in the last century, and some of the best results extant have been obtained by this method, which, however, is not so easy as it appears when the highest degree of accuracy is desired.

Lavoisier and Laplace, in 1780, devised the ice calorimeter which bears their name; and in a most interesting memoir, which is reprinted among Lavoisier's works, they show that they were familiar with the idea which in modern times is expressed as the principle of the conservation of energy. In this memoir they give the results of experiments, in which the specific heats of iron, mercury, and a few other substances are estimated with a very tolerable approach to accuracy. Although many of the metals were known to them, and supposing they had persisted in this work, it would not have been possible for them to make the discovery which was reserved for Dulong and Petit thirty-five years later, for the atomic theory had not then been conceived, and no elemental combining proportions had been determined.

Dulong and Petit* seem to have used at first the method of mixtures, and to have found, by direct experiment, that the specific heat of solids (metals and glass) increases with the temperature. They also studied (after Leslie) the laws of cooling of bodies; and two years after the publication of their first paper on the subject, they (Petit and Dulong, *sic*) arrived at the remarkable general expression which is associated with their names.†

After pointing out that all the results of previous experiments except those of Lavoisier and Laplace are extremely incorrect, they describe their own conclusions obtained by the method of cooling, conducted with many precautions to avoid error. The numerical expression of their experimental results is given in the following table:—

Copy of Table by Petit and Dulong.
(*Ann. Chim. Phys.*, 1819, x. 403.)

	Specific heats.	Atomic weights (o=1).	Atomic weight × specific heat.
Bismuth	0·0288	13·30	0·3830
Lead	0·0293	12·95	0·3794
Gold	0·0298	12·43	0·3704
Platinum	0·0314	11·16	0·3740
Tin	0·0514	7·35	0·3779
Silver	0·0557	6·75	0·3759
Zinc	0·0927	4·03	0·3763
Tellurium ..	0·0912	4·03	0·3675
Copper	0·0949	3·957	0·3755
Nickel	0·1035	3·69	0·3819
Iron	0·1100	3·392	0·3731
Cobalt	0·1498	2·46	0·3685
Sulphur	0·1880	2·011	0·3780

The statement of the relation indicated in the last column of figures is expresseed in the following words of the author, page 405: "Les atomes de tous les corps simples ont exactement la même capacité pour la chaleur."

Here the question rested, till resumed many years later (1840) by Regnault, who in his first memoir‡ pointed out the difficulties which attend the acceptance of the statement of Petit and Dulong in the form in which they gave it. He then discussed the three principal experimental methods, viz.: (1) fusion of ice; (2) mixture with water or other liquid; and (3) cooling; and decided in favour of the second, which he used throughout his researches. The general form of the apparatus used by the great physicist has been a model for the guidance of successive experimentalists since his time.

Another quarter of a century elapsed before the question of the specific heats of the elements was resumed by Hermann Kopp. His results were communicated to the Royal Society, and are embodied in a paper printed in the *Philosophical Transactions* for 1865. After reviewing the

* *Ann. Chim.*, 1817, vii., 144. † *Ibid.*, 1819, x., 395. ‡ *Ibid.*, 73, 5.

work of his predecessors, he described a process by which he had made a large number of estimations of specific heat, not only of elements, but of compounds of all kinds in the solid state. Concerning his own process, however, he remarks that "the method, as I have used it, has by no means the accuracy of that of Regnault" (p. 84).

In 1870 Bunsen introduced his well-known ice-calorimeter. This is an instrument in which the amount of ice melted by the heated body is not measured by collecting and weighing the water formed, but by observing the contraction consequent upon the change of state. The results obtained by Bunsen himself are uniformly slightly lower than those of Regnault for the same elements.

Since that time, experiments have been made by Weber, Dewar, Humpidge, and others, in connection especially with the influence of temperature in particular cases.

Setting aside the elements, carbon, boron, silicon, and beryllium, as providing an entirely separate problem, the question is whether the law of Dulong and Petit is strictly valid when applied to the metals. Kopp, in the discussion of his subject, came to the conclusion that it is not; but the grounds for this conclusion are unsatisfactory, since neither the atomic weights nor the specific heats were at that time known with sufficient accuracy. It has been customary to assume that the divergences from the constant value of the product, At. Wt. × Sp. Ht., are due partly to the fact that at the temperature at which specific heats are usually determined, the different elements stand in very different relations to their point of fusion; thus, lead at the temperature of boiling water is much nearer to its melting point than iron under the same conditions. The divergences have also been attributed to temporary or allotropic conditions of the elements. As to the relation to melting point, the specific heats of atomic weights seem to be practically the same in separate metals and alloys of the same which melt at far lower temperatures. For example, the atomic heat of cadmium is 6·35; of bismuth 6·47; of tin, 6·63; and of lead, 6·50; while the mean atomic heat in alloys of bismuth with tin and lead with tin ranges from 6·40 to 6·66 (Regnault), which is practically the same. Again, while the melting point of platinum is at a white heat, the metal becomes plastic at a low red heat, and yet the specific heat at this lower temperature is very little less than it is near the melting point. The properties of many other metals, notably zinc and copper, change considerably at temperatures far removed from their melting points without substantial change in their capacity for heat.

As to allotropy, it is a phenomenon which is comparatively rare among metals, and in the marked cases in which it occurs we have no information as to the value of the specific heats in the several varieties, such as the two forms of antimony and the silver-zinc alloy of Heycock and Neville, and they may be left out of account. Bunsen compared the so-called allotropic tin, obtained by exposing the metal to cold for a long time, and found it 0·0545 against 0·0559 for the ordinary kind (*Pogg. Ann.*, 141, 27). In dimorphous substances there is often no difference. Regnault found for arragonite 0·2086 and for calcite 0·2085 respectively. The differences between metals hammered and annealed, hard and soft, were also found by Regnault to be very small (*Ann. Chim.*, [3], ix.).

Hard steel ..	0·1175	Same, softened ..	0·1165
Hard bronze..	0·0858	Same, softened ..	0·0862

Kopp came to the conclusion, *first*, that each element in the solid state, and at a sufficient distance from its melting point, has *one* specific or atomic heat, which varies only slightly with physical conditions; and *secondly*, that each element has essentially the same specific or atomic heat in compounds as it has in the free state. This last is practically identical with the statement which is known as Neumann's law. With Kopp's conclusion I agree, but, from some of Regnault's results coupled with my own, the effect of *small* quantities of carbon and perhaps of sulphur upon the specific heats of metals is greater than has been supposed. If we take the results of Regnault and of Kopp and combine them with the most accurately known atomic weights, the products are still not constant.

Atomic Weights most accurately known (1897) *combined with Specific Heats.*

	A.W. (H=1)	S.H. Regnault.	S.H. Kopp.	At. Ht. Regnault.	At. Ht. Kopp.
Copper	63·12	0·09515	0·0930	6·01	5·87
Gold	195·74	0·03244	—	6·35	—
Iron	55·60	0·11379	0·1120	6·33	6·23
Lead	205·36	0·03140	0·0315	6·45	6·47
Mercury liq. ..	198·49	0·03332	—	6·61	—
Mercury −78° to +10° sol... ..	198·49	0·03192	—	6·34	—
Silver	107·11	0·05701	0·0560	6·11	6·00
Iodine	125·89	0·05412	—	6·81	—

The "Law" of Dulong and Petit is therefore only an approximation; but this may perhaps be due to inaccuracy in the estimation of the specific heat, owing to impurity in the material used. That is the problem which I have endeavoured to solve.

The introduction by Prof. J. Joly of a new method of calorimetry, which depends upon the condensation of steam upon the cold body, and the excellent results obtained by the author in the use of the differential form of his instrument (*Proc. R. S.*, xlvii., 241), led me to think that with due attention to various precautions—such as exact observations of the temperatures, and practice in determining the moment at which the increase of weight due to condensation is completed—results of considerable accuracy might be obtained.

The problem is to find two elements, very closely similar in density and melting-point, which can be obtained in a state of purity, and then to determine with the utmost possible accuracy the specific heat of each under the same conditions.

The two metals cobalt and nickel were selected for the purpose. They were examined by Regnault, but the metals he used were very impure.

The cobalt employed in my experiments was prepared by myself. For the nickel I am indebted to Dr. Ludwig Mond. Both were undoubtedly much more nearly pure than any metal available in Regnault's time. The results obtained are as follows:—

Specific Heats of Cobalt and Nickel.

Pure fused.

Cobalt, S. G. 21°/4°, 8·718.	Nickel, S. G. 21°/4°, 8·790.	
0·10310		
0·10378		
0·10310	0·10953	too high?
0·10355	0·10910	too high?
0·10373	0·10930	too high?
0·10362		
Arith. mean .. 0·10348	.. .. 0·10931	

The value arrived at for cobalt is much lower than that (0·1067) derived from Regnault's experiments, while that for nickel is practically identical with Regnault's, which is 0·1092. This is certainly too high.

Further experiments will be made, because a single well-established case of this kind is sufficient to decide the question. Already, however, I feel certain that Kopp's conclusion is right, and that the law of Dulong and Petit, even for the metals, is an approximation only, and cannot be properly expressed in the words of the discoverers. For, although the exact values of the atomic weights of these two elements, cobalt and nickel, are not

known, it is certain that they are not so far apart as would be implied by these values for the specific heats.

Two other examples of somewhat similar kind are shown by gold and platinum, copper and iron.

For the gold I naturally applied to my colleague, Prof. Roberts-Austen. The platinum I prepared from ordinary foil, by re-solution and re-precipitation as ammonio-chloride, and subsequent heating. Both metals were fused into buttons before use. The atomic heats come closer together than those of Co and Ni.

Copper and iron differ considerably in melting-point, but both at the temperature of 100° are far removed from even incipient fusion. The copper was prepared from pure sulphate by electrolysis, the iron by reduction of pure oxide in pure hydrogen. Notwithstanding all our care, it was disappointing to find it contained 0·01 per cent of carbon, the source of which I am at a loss to explain. This iron is purer than any examined by Regnault or Kopp.

Specific Heats of Gold and Platinum.

Pure fused.

Gold, S. G. 18°/18°, 19·227.		Platinum, S. G. 18°/18°, 21·323.	
0·03052		0·03147	
0·03017		0·03150	
0·03035		0·03144	
Arith. mean ..	0·03035	Arith. mean ..	0·03147
Atomic heat ..	5·94	Atomic heat ..	6·05

Specific Heats of Copper and Iron.

Fused.

Copper (pure) S. G. 20°/20°, 8·522		Iron, S. G. 15°/15°, 7·745,	
0·09248		contains 0·01 p.c. copper.	
0·09241		0·11022	
0·09205		0·11037	
0·09234			
Arith. mean ..	0·09232	Arith. mean ..	0·011030
Atomic heat ..	5·83	Atomic heat ..	6·13

The differences observed between cobalt and nickel, and between gold and platinum, are manifestly not due to allotropes or to differences of melting point, which in these cases can have no effect on the result. So large a difference must be due to peculiarities inherent in the atoms themselves; and differences of atomic heat are to a certain extent comparable with the differences observed in other physical properties, which, like specific volume, specific refraction, &c., are approximately additive.

If we try to think what is going on in the interior of a mass of solid when it is heated, the work done is expended not only in setting the atoms into that kind of vibration which corresponds to rise of temperature, that is, it makes them hotter, but partly in separating the molecules or physical units from one another (=expansion) and partly in doing *internal* work of some kind, the nature of which is not known. A difference between metals and non-metals has been brought out by the researches of Heycock and Neville, who find that metals dissolved in metals are generally monatomic; whereas it is generally admitted that iodine, sulphur, and phosphorus in solution are polyatomic. It is moreover remarkable that, although in respect to specific heat each element in a solid seems to be independent of the other elements with which it is associated, when the elementary substances are vapourised some rise in separate atoms like mercury, some in groups of atoms like iodine, sulphur, arsenic, and phosphorus, and as the temperature is raised these groups are simplified with very varying degrees of readiness.

The two metals, cobalt and nickel, with which I began my inquiry, have very nearly the same atomic weight, the value, 58·24 for nickel and that for cobalt 58·49, being calculated by F. W. Clarke from the results of a great many analyses by many different chemists. They are so close together that for a long time they were regarded as identical, and Mendeléef does not hesitate even to invert the order by making Co=58·5 and Ni=59. These metals nevertheless, differ from each other in several very important chemical characters. Nickel, for example, forms the well known and highly remarkable compound with carbonic oxide discovered by Dr. Mond. Cobalt, on the other hand, produces many ammino-compounds to which there is nothing corresponding among the compounds of nickel.

Having put aside the common excuses for the observed divergences from the constant of Dulong and Petit, we are compelled to look round for some other hypothesis to explain them.

The constitution of carbon compounds is now accounted for by a hypothesis concerning the configuration of the carbon atom introduced by van 't Hoff and Le Bel twenty-five years ago, and which is now accepted by the whole chemical world. It seems not unreasonable to apply a similar idea to the explanation of those cases of isomerism which have been observed in certain compounds of the metals, notably chromium, cobalt, and platinum. This has already been done by Professor Werner, of Zürich. If the constitution of compounds can be safely explained by such hypothesis, this implies the assumption of peculiarities in the configuration of the individual constituent metals around which the various radicles are grouped in such compounds; and hence peculiarities in the behaviour of such metals in the elemental form may possibly be accounted for. For the atom of cobalt Professor Werner employs the figure of the regular octahedron. For nickel, therefore, which differs from cobalt in many ways, a different figure must be chosen. This, however, is for the present a matter of pure speculation.

THE ESTIMATION OF SUCCINIC ACID IN THE PRESENCE OF TARTARIC AND LACTIC ACIDS.

By MM. BORDAS, JOULIN, and DE RACZKOWSKI.

WHEN we add a concentrated solution of nitrate of silver to a solution containing these three acids in the state of soluble neutral salts, the succinic acid is precipitated integrally, the tartaric acid partially, while the lactic acid remains in solution on account of the different solubilities of these three salts of silver.

This being admitted, the following is the manner in which we effect the estimation:—

The solution containing the three acids is exactly neutralised by means of a decinormal solution of potash. We note the number of cubic centimetres necessary, we then add an excess of a concentrated solution of nitrate of silver. The precipitate is filtered and washed until a drop of the filtrate is no longer precipitated by neutral chromate of potassium. Under these conditions the succinate of silver *only* remains on the filter, the tartrate of silver being completely dissolved by the wash waters.

The washed precipitate is transferred to a flask by means of a fine jet of water from the wash bottle, and two drops of a neutral solution of chromate of potassium are added; this decomposes the succinate of silver in suspension and forms chromate of silver. We then add such a quantity of a decinormal solution of sodic chloride that the precipitate becomes white and the liquid takes a yellow tint. It suffices then to pour in a solution of nitrate of silver, also decinormal, until the liquid commences to take a reddish-brown colour.

By subtracting the number of cubic centimetres of nitrate of silver from that of the decinormal chloride of sodium, we obtain the volume of the decinormal solution of nitrate of silver necessary to precipitate the amount of succinic acid present. 1 c.c. of this solution corresponds

to 0·0059 of succinic acid. As, on the other hand, it is an easy matter to estimate the tartaric acid, the lactic acid can be obtained by difference.—*Journ. de Pharm. et de Chim.*, Series 6, vol. vii., No. 9.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 16th, 1898.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 9).

*93. "*Reversible Zymohydrolysis.*" By Arthur Croft Hill, B.A.

This investigation was undertaken to ascertain whether zymohydrolysis is a reversible process or not. The hydrolysis of maltose by maltase was selected for the purpose, the enzyme being obtained by extracting dry and finely powdered low-fermentation yeast, which had been heated under certain precautions, as detailed in the paper. It was found that the extract could be sterilised without destruction of its activity by filtration through a Pasteur-Chamberland filter.

The analytical methods for estimating the extent of hydrolysis were (1) determination of the cupric-reducing power of the mixed sugars; (2) determination of the specific rotatory power. The details of the methods and limits of accuracy are dealt with fully in the paper. To simplify calculations, maltose is reckoned as maltose hydrate, $C_{12}H_{22}O_{11},H_2O$.

The zymohydrolysis of maltose into glucose is hindered by the presence of glucose and is incomplete, and both these effects are more marked the more concentrated the solution of sugar. The retardation is shown by two sets of experiments. In the first set, the initial velocities of conversion are compared in a solution of maltose of a certain concentration with that in a solution of half maltose and half glucose of like total concentration. The ratio of these velocities should be not greater than 2, if the glucose were without influence; actually it is much greater, being about 3 for a 4 per cent, and 4·85 for a 20 per cent sugar concentration. In the second set, the time curves are compared for two flasks, each containing initially the same concentration of maltose, while to one glucose has been added in equal concentration. If glucose were without influence, the time curve of conversion of maltose into glucose should be identical for each flask, but a much slower conversion occurs in that containing the added glucose, and the effect is much more marked with a total sugar concentration of 20 per cent than with one of 4 per cent.

When the enzyme acts in a 20 per cent solution of glucose, a small reverse action can be detected by the polarimeter. With a 40 per cent concentration, the reverse action is well marked, and when sufficient time has been allowed for this action, which is a slow one, to approach completion, the reversion indicated by the change in rotatory and cupric-reducing powers amounts to 15 per cent of the sugar. Control flasks show no change. With a 40 per cent solution of sugar, of which 75 per cent was glucose and 25 per cent maltose (hydrate), hydrolysis proceeded till 83·25 per cent of the total sugar was glucose, and the equilibrium point, therefore, for this concentration is not far from 84 parts glucose to 16 parts maltose (hydrate). Equilibrium points for various concentrations have been determined; and it is found that in dilute (2 per cent) solutions hydrolysis is practically complete. The same equilibrium point is approached either with a solution of maltose or with one of glucose of the same concentration.

Maltose has been detected as a product of the reverse action by the use of phenylhydrazine. An osazone having a greater solubility in boiling water than glucosazone has been separated, and this crystallises in plates, has the same percentage of carbon and nitrogen as maltosazone, but melts at a temperature somewhat lower than maltosazone from pure maltose, though not lower than that prepared from ordinary maltose under similar conditions, viz., from a mixture of maltose with excess of glucose to which some boiled enzyme solution has been added, the proteid being then removed as completely as possible before treatment with phenylhydrazine. The synthesised maltose has not yet been isolated, but it is considered that the evidence of its presence, coupled with the increase of optical rotatory power, and corresponding decrease in cupric-reducing power observed in concentrated glucose solutions in the presence of maltase, justify the conclusion that the zymohydrolysis of maltose is a reversible process.

Discussion.

Dr. Horace Brown congratulated the author on the important results he had obtained, and stated that, although some such reversed action was recognised when dextrose is acted on by dilute acids, this was the first time that anything of the kind had been shown to occur during prolonged enzyme action. He had been privileged to see the details of the author's work whilst it was in progress, and was quite satisfied that a reversal had really taken place. The alteration in optical and reducing properties, and the appearance of the osazone pointed strongly to the reversed product being ordinary maltose, but until this was isolated, and such isolation ought not to present any insuperable difficulties, he did not feel quite satisfied as to its nature. It could not be identical, however, with the isomaltose obtained by Emil Fisher by the action of acid on dextrose.

Mr. Ling thought that additional evidence was necessary before it could be definitely concluded that maltose was produced from glucose, and, as a possible means of deciding the question, suggested converting the product into acetyl derivatives instead of into osazones. Octacetylmaltose was a well characterised compound, and could, he thought, be separated from the acetyl derivatives of glucose.

94. "*The Solubility of Isomeric Substances.*" By James Walker, PhD., D.Sc., and John K. Wood, B.Sc.

In continuation of a research by Carnelley and Thomson (*Trans.*, 1888, 53, 782), the authors have investigated the solubility of the hydroxybenzoic acids, and the isomeric ureas, $C_7H_8N{\cdot}CO{\cdot}NH_2$, in various solvents.

The values obtained for the solubility of salicylic acid at different temperatures are one-third less than the values given by Bourgoin. The variation of the solubility of the hydroxybenzoic acids in water with the temperature is expressible up to 50° by a formula of the type proposed by Nordenskjöld, the equations being, for the ortho-acid, $\log S = 0{\cdot}01556t - 1{\cdot}0458$; for the meta-acid, $\log S = 0{\cdot}01793t - 0{\cdot}4188$; and for the para-acid, $\log S = 0{\cdot}0227t - 0{\cdot}7972$. With benzene as solvent, a formula of this type does not express the variation of the solubility with the temperature.

Congo red was found to be the best acidimetric indicator for salicylic acid and its isomerides.

The rule that the order of fusibility of isomeric substances is also the order of their solubility does not hold good for the hydroxybenzoic acids, but it is in general applicable to benzyl urea and its isomerides.

The rule that the order of solubility of isomerides is independent of the solvent is not strictly applicable in either of the cases investigated. The constancy of the solubility ratio observed by Carnelley and Thomson for para- and meta-nitraniline is not found either with the acids or with the ureas. The solubility ratios of the hydroxybenzoic acids in the same solvent vary considerably with the temperature.

95. "*Note on Nitration and Substitution in Nitro-compounds.*" By ARTHUR LAPWORTH, D.Sc., and CHARLES MILLS.

It is known that (1) nitro-compounds yield chiefly meta-derivatives with most substituting agents, but orthonitrophenols when acted on by alkaline ferricyanide; (2) ortho- and para-chloronitrobenzene form the corresponding nitrophenols by interaction with alkalis, whilst the meta-compound is not affected; (3) ortho- and para-ethoxynitrobenzene are converted into the corresponding nitranilines on treatment with ammonia, but the meta-derivative is not affected. The authors consider that these facts are in complete accordance with the view of substitution advocated by one of them (*Trans.*, 1898, 73, 445), namely, that substitution in nitro-compounds is largely due to the occurrence of successive, irreversible, desmotropic changes in products formed by the addition of the acting agent to the side group.

In the hope of showing that when acid oxidising agents act on nitro-compounds, ortho- or para-nitrophenols, if any, would be produced, the authors undertook the investigation of an acid substance formed under certain conditions during the nitration of toluene. As ortho- and para-nitrotoluenes are the chief products of that reaction, it was thought probable that this substance had been formed from one of these. Examination showed, however, that oxidation of toluene had doubtless been the first action, as the substance was identified as dinitro-paracresol [Me: OH : $(NO_2)_2$=1 : 4 : 3 : 5], and thus contained both nitro-groups in meta-positions relatively to the methyl radicle.

96. "*Hydroxydibromocamphorsulphonic Acid. A Correction.*" By ARTHUR LAPWORTH, D.Sc., and F. STANLEY KIPPING, D.Sc., F.R.S.

In a paper on "Sulphocamphoric Acid and other Derivatives of Camphorsulphonic Acid" the authors described as "hydroxydibromocamphorsulphonic acid, $C_{10}H_{14}Br_2SO_5$," a compound obtained by oxidising ammonium *a*-bromocamphorsulphonate with nitric acid (*Trans.*, 1897, 71, 19). This composition was assigned to the oxidation product in question, partly from the results of analyses, partly from the study of a well-defined crystalline sulpholactone, $C_{10}H_{12}Br_2SO_4$, which was obtained simultaneously with the acid, and into which the acid was found to be convertible under certain specified conditions. At the same time, it was admitted that no direct evidence of the presence of a hydroxyl group in the acid had been obtained, and that, although the conversion of the acid into the lactone had been accomplished, the method by which this change was brought about was difficult to explain.

Further investigation has shown that the supposed "hydroxy-acid, $C_{10}H_{14}Br_2SO_5$," is in reality a *hydrated dibromocamphorsulphonic acid*, $C_{10}H_{14}Br_2SO_4,H_2O$, so that its conversion into the lactone by the process employed (boiling with aqueous silver nitrate) is now explained as a simple oxidation followed by elimination of the elements of water. The analyses already referred to gave results agreeing just as well with those required by the new (C=29·4; H=3·9; Br=39·2; S=7·8 per cent) as with those calculated for the original formula, and further analyses have given equally satisfactory results (C=29·7; H=3·8; Br=39·4). The *anhydrous acid* was only obtained with difficulty owing to the water of crystallisation in the hydrated compound being very obstinately retained; it crystallised from petroleum and ether in slender prisms melting with decomposition at 245—252°, and on analysis gave the following results ($C_{10}H_{14}Br_2SO_4$ requires C=30·8; H=3·6; Br=41·0. Found C=30·5; H=3·6; Br=41·2 per cent).

One of the authors has now obtained the acid by a method which confirms this view of its composition, and its investigation is being continued.

97. "*Enantiomorphism.*" By F. STANLEY KIPPING, D.Sc., F.R.S., and WILLIAM JACKSON POPE.

The authors have previously shown (*Proc.*, 1896, 12, 249) that, on crystallising the cubic tetartohedral sodium chlorate from aqueous solutions containing various optically active carbohydrates, the two enantiomorphously related crystalline forms of sodium chlorate are deposited in different numbers; numerical data respecting the ratios of the numbers in which dextro- and lævo-crystals of sodium chlorate separate from solutions containing dextroglucose, mannitol, dulcitol, and isodulcitol are now given. A saturated solution of sodium chlorate containing 200 grms. of *d*-glucose per litre deposits on crystallisation an average of 31·75 per cent of dextro- and 68·25 per cent of lævo-crystals of sodium chlorate by number; results showing that a similar enantiomorphous influence is exercised on the crystallisation of sodium chlorate by other carbohydrates are also given.

Data have also been obtained respecting the proportion in which dextro- and lævo-crystals of sodium chlorate separate from pure aqueous solutions; the examination of a large number of crops of crystals shows that 50·08 ± 0·11 per cent of the deposited crystals are dextrorotatory.

98. "*Azobenzene Derivatives of Chrysin, Euxanthone, Gentisin, and Morin.*" By A. G. PERKIN.

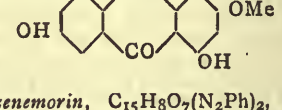
It has been previously shown that apigenin, the colouring matter of parsley, *Apium petroselinum* (*Trans.*, 1897, 71, 805), forms a disazo-derivative, and that during its purification with nitrobenzene and acetic a by-product is obtained, which is evidently an acetyl compound (*Proc.* 1897, 13, 54). Thus prepared, the latter is apt to be impure, and is best formed by the prolonged digestion of disazo-benzeneapigenin with boiling acetic anhydride. It forms orange-red needles melting at 277—280° when rapidly heated, and in general properties is almost indistinguishable from the disazo-compound itself.

Chrysin, the colouring matter of poplar buds, yields a *disazo*-derivative, $C_{15}H_8O_4(N_2Ph)_2$, which crystallises in orange-coloured needles, melts at 250—252°, and is insoluble in alkaline solutions. It contains no free hydroxyl groups.

The diazobenzene groups in these compounds are thus adjacent to the two hydroxyl radicles of the phloroglucinol nucleus, and the results harmonise with previous work which indicated that apigenin is a hydroxychrysin.

Euxanthone, derived from the Indian dye-stuff "purree," yields *disazobenzene-euxanthone*, $C_{13}H_6O_4(N_2Ph)_2$, which crystallises in brick-red needles, melts at 249—250°, and is almost insoluble in alkalis. Acetic anhydride converts it into a *diacetyl* compound, $C_{13}H_4O_4Ac_2(N_2Ph)_2$, which forms olive-coloured needles and melts at 197—199°.

From gentisin, *disazobenzenegentisin*, $C_{14}H_8O_5(N_2Ph)_2$, is obtained. This crystallises in orange-red needles, melts at 218—220°, and yields a *diacetyl* derivative, $C_{14}H_6O_5Ac_2(N_2Ph)_2$. These results indicate that the methoxyl group in gentisin has the following position:—



Disazobenzenemorin, $C_{15}H_8O_7(N_2Ph)_2$, a red-brown, crystalline powder, is formed in very small quantity by the interaction of diazobenzene sulphate with morin in alkaline solution. No trisazo-compound could be obtained.

99. "*Constituents of the Indian Dyestuff 'Waras.'*" By A. G. PERKIN.

Waras is a purplish powder which covers the seed pods of *Flemingia congesta*, an erect, woody shrub of Africa and India. In its general properties and microscopic appearance it closely resembles kamala (*Mallotus Philippinensis*) previously investigated (*Trans.*, 1893, 63, 975; 1894, 65, 232). For the supply of material, which is very difficult to procure, the author is indebted to the authorities of the Imperial Institute.

Flemingin, $C_{12}H_{12}O_3$, the principal crystalline constituent, was obtained as an orange-red powder consisting of small, prismatic needles melting at 171—172°. In appearance and numerous properties it resembles the rottlerin of kamala, but is distinguished from this by its solubility in alcohol, and by the browner tint of its alkaline solutions. In an alkaline bath, it dies silk a golden yellow, and is a stronger dyestuff than rottlerin. On fusion with alkali, it gave acetic acid, salicylic acid, and an acid of higher melting point which was not identified.

Homoflemingin (C=69·97; H=5·75), present only in minute quantity, forms glistening, yellow needles, melts at 164—166°, and possesses properties resembling those of flemingin.

The *resin of high melting point*, ($C_{12}H_{12}O_3$, forms a brick-red powder soluble in alkali, with a deep brown tint, and yields acetic and salicylic acids on fusion with alkali. It dies silk in shades which are redder than those produced by flemingin.

The *resin of low melting point*, $C_{13}H_{14}O_3$, is a deep orange-brown, transparent mass which melts below 100°, is soluble in alkali with an orange-brown colour, and closely resembles the resin of low melting point of kamala. On fusion with alkali, acetic and salicylic acids are obtained, and on boiling with nitric acid (sp. gr. 1·5) oxalic acid is formed.

From numerous characteristic reactions described in the paper, it is concluded that the above substances are closely related to, though not identical with, those present in kamala.

Waras dyes silk a golden yellow shade, and is a much stronger dye-stuff than kamala.

100. "*Note on the Oxidation of Charcoal by Nitric Acid.*" By G. DICKSON, M.A., and T. H. EASTERFIELD, M.A., Ph.D.

Well-burnt charcoal reacts readily with fuming nitric acid, the action being accompanied by a considerable rise of temperature. When boiled for 24 hours with fuming nitric acid, the charcoal goes entirely into solution, and on dilution with water a black, amorphous substance is precipitated, whilst mellitic and non-crystalline acids remain in solution. The black, amorphous substance resembles the "mellogen" of Bartoli and Papasogli (*Gazz.*, 1882, 12, 117), it is easily soluble in alkali, and on oxidation by alkaline permanganate yields oxalic and mellitic acids in about equal proportions.

From charcoal, 25 per cent. of its weight of crystalline ammonium mellitate can be obtained by the following process. The charcoal is boiled with fuming nitric acid for 24 hours and further oxidised by adding potassium chlorate to the boiling solution; the organic acids, after precipitation as barium salts, are converted into ammonium salts. The yield of mellitic acid varies only slightly, whether the charcoal contains 2 or only 0·2 per cent of hydrogen. Coal under similar conditions gives only a small yield of mellitic acid.

Even nitric acid of sp. gr. 1·1 can oxidise well-burnt charcoal. After boiling continuously for seven days, the charcoal is changed to a black, impalpable mud, soluble in alkali. The nitric acid solution contains mellitic but no oxalic acid.

Banquet to Past Presidents.

The banquet to Past Presidents, unavoidably postponed from June 9th, has been finally fixed by the Council for Friday, November 11th.

Royal Institution.—A General Monthly Meeting was held on the 4th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The special thanks of the Members were returned for the following donations to the Fund for the Promotion of Experimental Research at Low Temperatures:—Sir Frederick Abel, Bart., K.C.B., £100; Sir Andrew Noble, K.C.B., £100; Sir John Brunner, Bart., M.P., £50.

CORRESPONDENCE.

THE NEW GASES.

To the Editor of the Chemical News.

SIR,—In a paper read before the Royal Society on June 16th, by Prof. Ramsay and Mr. Travers, in describing a supposed new gas, they mention the existence of a brilliant yellow line not identical with sodium, helium, or krypton, having a wave-length of 5849·6: this line they call D_5, and propose the name "neon" for the element which it indicates.

Now, in the *Comptes Rendus* (cxxvi., p. 1762), in a paper by Messrs. Ramsay and Travers, the same line D_5, wave-length 5849·6, is again described, but in this case they propose the name "metargon" for the new gas. Surely there must be a misprint in one paper or the other. In the Royal Society paper both "neon" and "metargon" are fully described, and a number of lines with their wave-lengths are given for each gas; but in the *Comptes Rendus* paper "neon" is passed over very lightly, and practically all the figures given refer to what is there called "metargon." These discrepancies are further accentuated by the densities given: in the Royal Society paper, the gas with the line D_5 called "neon" is given a density of 14·67; while in the *Comptes Rendus* paper, the gas with the line D_5 called "metargon" has a density of 19·87. It is obvious that D_5, wave-length 5849·6, cannot belong to both gases. To which does it belong?—I am, &c.,

PUZZLED.

THE NEW GASES.

To the Editor of the Chemical News.

SIR,—In 1892 Dr. Hussein Off and I read before the Chemical Society a paper (4½ pages long) entitled "Indications of a possible New Element in an Egyptian Mineral," and this was the only commmunication on the subject that I wrote or was responsible for; a description of this as "an elaborate paper to announce the discovery of a new element" is hardly accurate.

It is still more inaccurate to say that Prof. Ramsay has nothing to show as to the existence of the new gases but spectral lines, and this is the whole basis of "Suum Cuique's" attack: reference to the papers of Prof. Ramsay and his colleagues show that the attempts made to split up the new gases have revealed properties sufficient without the spectra to afford strong evidence that the gases are really new. Propositions with an inaccurate basis need no assailing; they fail naturally.

I believe the impression that I had gathered, that Prof. Ramsay had the possible mixed nature of argon constantly before his mind, to be correct; if not, why should he have worked so assiduously, and, as we now learn, successfully, to split it up? I have no difficulty in reconciling this impression with the fact that argon was declared to be an element. This is but an instance of the inadequacy of language to express ideas; we have defined an element as a body which has not, by any possible means in our power, been split up, and argon, when it was declared to be an element, conformed strictly to that definition. We do not vilify the early workers on didymium. We all accept the expression "elements in an impure state" as a reasonable phrase, and these words imply the acceptance of the possibility of an element being mixed with other substances, though not losing thereby its elementary character.

It appears that, in his first letter, when "Suum Cuique" was only considering Prof. Ramsay's work, he could see no merit in the discovery of argon; in his second letter, after being reminded of Lord Rayleigh's share, he admits that there is much merit. It is further

stated that Prof. Ramsay is not the chemist with whom Lord Rayleigh would have associated himself had he been left a free agent. It looks very much as if Prof. Ramsay's scientific work is to be belittled, because exception is taken to his conduct from an ethical standpoint. Would it not be more manly to state any real grounds of complaint that may exist, than to assail his work inaccurately and anonymously?

I regret that I made the groundless and utterly erroneous assumption that "Suum Cuique" was not acquainted with the classical experiment of Cavendish; seeing that it is by no means the best known of his experiments, I imagined that probability was against his having known it. I am sorry that, in attributing ignorance to him, I used the unnecessary word "blissfully," and admit that the annoyance I must have caused him justifies his free use of adjectives.

In conclusion, Sir, I hope, as a student of Prof. Ramsay's work, that he and his colleague will not be led by this discussion to defer publication of any more results till they have isolated all the gases of the atmosphere in a state of absolute purity, and have determined the whole of their properties: I believe I shall voice the opinion of a considerable section, if I say that the publication of their results as they get them will be welcomed as an addition to the world's knowledge.—I am, &c.,

H. Droop Richmond.

St. Margaret's, July 5, 1898.

MOLECULAR DETERMINATIONS IN SOLUTIONS.

To the Editor of the Chemical News.

Sir,—If it be the case, as mentioned in the paper by Messrs. Jones and King (Chemical News, lxxvii., p. 243), that the boiling-point method is the only one at present applicable to the generality of solvents, it may doubtless be of interest to describe a process which under some circumstances may be found useful. I tested it some time ago with satisfactory results. It is generally applicable to all, or at all events to the more volatile solvents, not limited strictly to one particular temperature, but workable for a considerable range below the boiling-points. It is independent of any constants special to different liquids. It is, moreover, capable of being applied rapidly, and with no further equipment than is found in every laboratory.

The principle of the method is the measurement of vapour pressure by means of evaporation. With a liquid evaporating, the number of vapour molecules per unit volume of the space above will be proportional to the pressure of the vapour. If the space—*i. e.*, if the air—above the liquid is renewed as fast as saturated, the number of molecules carried off will be proportional to the vapour pressure. This will also be true when different liquids are compared, and when a pure liquid is compared with the same liquid containing a non-volatile dissolved substance. The presence of substances in solution lowers the pressure, the amount evaporated is diminished, the diminution of the quantity evaporated is a measure of the diminution of pressure.

To apply this in practice it is, of course, not sufficient simply to leave the pure liquid and the solution to evaporate under similar conditions of pressure, temperature, and extent of exposed surface. The changes of concentration at the surface of the solution are too tardily counteracted by diffusion; the decrement of evaporation is far greater than it would be if the process were simply determined by the average concentration.

A uniform concentration throughout the liquid and a uniform evaporation, however, can be secured by blowing through the solution and the pure solvent approximately equal quantities of air.

A process of this sort, described by Ostwald, was put in practice by Walker, and by Will and Bredig, but it involves too great an expenditure of time; even for a liquid as volatile as alcohol a single experiment occupied twenty-four hours.

By the method here described a single experiment occupies, when once the apparatus has been constructed, about twenty minutes, and it can be repeated in ten. It consists of a couple of well-corked test-tubes, each fitted like a Woulff's bottle, with a tube dipping nearly to the bottom, and a short outlet tube with one bend; in one of these test-tubes is placed the solution, in the other the pure solvent. One of the outlet tubes is put in communication with an aspirator, and the dipping-tube of the other test-tube in communication with the air-cistern—a closed vessel into which the water of the aspirator is allowed to run. Thus a current of air is drawn through the liquid in the one test-tube and driven through the other, the quantities of air in each case being approximately equal. This approximation is sufficiently exact when by changing the connections the current, under the same conditions, has been reversed. The difference still remaining is due to the difference of vapour pressure between the two liquids, and it may be got over by saturating the air with the pure liquid, as under aspiration it issues from the test-tube containing the dissolved substance. The advantage seemed, however, on trial to be more theoretical than practical.

The temperature was kept uniform by means of a (generally cold) water-bath, in which the test-tubes stood. To keep them dry, for greater convenience and correctness of weighing, they were surrounded by two close-fitting cylinders of thin copper, blocked at the bottom, which were inserted in the closed top of the water-bath; thus the test-tubes were not in contact with water or water-vapour.

The test-tubes were fitted with rubber corks of two holes; but in the case of carbon disulphide, benzene, and such solvents as rapidly pass through indiarubber, these had to be replaced by ordinary corks capped with sealing-wax. The weighing of the test-tubes and contents was done with the corks and glass fittings *in situ*. Special precautions in the case of volatile solvents had to be taken with the capping of the small glass tubes. Part of an old Kipp's apparatus was extremely serviceable as aspirator; the construction enabled the amount of water passed to be very accurately controlled.

For water and liquids of low volatility the whole of the water-bath with the test-tube should be put in a water-oven, and so arranged that the connections can be changed on the outside. This will prevent the solvent from condensing on the outlet tubes, which it would otherwise do if only the water-bath were heated.

With such apparatus, when both test-tubes are charged with the pure solvent the difference of the amount evaporated ought not to differ by 1/10th per cent. For the purpose of the experiment the air passing must be saturated. This renders the application of heat necessary in the case of liquids of non-volatility equal to toluene. For such a liquid as carbon disulphide it made no difference whether the dipping-tubes passed 9 c.m. or 1·5 c.m. into the liquid; but, of course, for the sake of equalising the pressure, both dipping-tubes should go to the same depth (they may be graduated for the purpose). This question of pressure seems to prevent the use of *two blow-throughs*, — with one suction arrangement and one *blow-through* it is greatly neutralised.

Where advisable it is possible to substitute any other gas for air. Of course the air must be dried as it passes from the air-cistern. The rate of air-flow is without effect on the result, but splashing inside the test-tubes must be avoided.

Of course the concentration of the solution varies during the experiment, the average concentration has to be calculated for. Not more than 1/10th of the whole solution need generally be evaporated.

The formula for calculation will be as follows :—

$$\frac{\text{Difference of amount evaporated in the two tubes.}}{\text{Amount evaporated in the solution.}} = \frac{\text{Number of molecules of dissolved substance.}}{\text{Number of molecules used to dissolve it.}}$$

Or if q be the amount evaporated from the pure solvent, q' the amount evaporated from the solution, N the number of gramme-molecules of solvent in the solution, n the number of gramme-molecules of the dissolved substance—

$$\frac{q-q'}{q'} = \frac{n}{N}$$

There is no constant to be varied for each liquid.

I offer this method to your readers believing that it supplies a rapid and sufficiently accurate means of determining molecular weight, and that from its nature it is also capable of development and improvement so as to attain to the very highest accuracy.—I am, &c.,

P. J. Beveridge, M.A., B.Sc.

St. Helen's, June 28, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 19, May 9, 1898.

Method for the Detection and Estimation of Carbonic Oxide in the presence of Traces of Carburised Gas in the Atmosphere.—Armand Gautier.—To determine the amount of carbonic oxide in air, the air, previously deprived of all dust, acid gases, and water, is passed through two tubes, the first 0·28 m. in length, containing iodic anhydride, and the second 0·18 m. long, containing pure powdered copper (reduced by hydrogen): these tubes are sealed together in such a manner that they can both be placed in an air-oven and heated to 100—105°. This amount of copper is quite sufficient to take up all the iodine given off, no matter how dilute the vapour may be. A number of experiments which follow show that this method is sure and convenient in the ordinary cases when the air, or other inert gas, contains not more than 1/10,000th part of carbonic oxide. But the figures given, however satisfactory they may be in an ordinary case, may not be so certain when there is only a trace of carbonic acid present. To settle this point another potash tube was added at the end of the copper tube for the purpose of collecting the last traces of iodine, and then, for eight hours, a quantity of air containing enough CO_2 to set free nearly 15 m.grms. of iodine was slowly circulated through the apparatus.

The iodide stopped by the copper was .. .. = 14·72 m.grms.
And that which passed the copper, but was stopped by the potash, was .. .. = 0·011 ,,

The author then goes on to describe further experiments for the purpose of eliminating any hydrocarbides which may be present.

Vaporisation of Iron at the Ordinary Temperatures.—H. Pellat.—The following experiment whs made by the author:—A small iron ring was laid directly on the sensitive surface of a bromo-gelatin plate; at its side another similar ring was placed, but separated from the sensitive surface by a very thin sheet of microscopic *cover* glass; the latter was covered by a bell-jar fastened to the plate with paraffin as in M. Becquerel's sxperiment. The whole was left in the dark from December 24, 1897, until April 27, 1898. After developing the plate, it was found that the iron ring under the jar had made no impression, but that the ring placed directly on the sensitive film had produced an image of a slightly larger size than the ring itself, and therefore extending beyond the line of contact. This experiment shows that the phenomenon is not due to radiations, but to a volatile body produced by the iron.

On a Borocarbide of Glucinum.—P. Lebeau.—Already inserted in full.

Some Halogen Salts of Lead.—V. Thomas.—The object of this note is the study of the chloroiodides of lead. The action of boiling hydrochloric acid on iodide of lead always gives rise to a chloroiodide, PbICl. If iodide of lead reacts on a chloride, or chloride of lead on an iodide, the result is always the same,—PbICl is formed. The existence of the chloroiodide as a well-defined chemical compound is shown by the product of oxidation it is able to form when treated with peroxide of nitrogen.

Thermic Data relating to Ethyl-malonic Acid. Comparison with its Isomers, Glutaric and Methyl-succinic Acids.—G. Massol.—Anhydrous ethyl-malonic acid dissolves in water with a heat of absorption of −2·96 cals. The heats of neutralisation are—for $C_5H_7O_4K$, +14·08 cals., and for $C_5H_6O_4K_2$, +13·80 cals. The heat of formation of a solid neutral salt, from the solid acid and base, is—

$$C_5H_8O_4 \text{ sol.} + 2KOH \text{ sol.} = C_5H_6O_4K_2 \text{ sol.} + 2H_2O \text{ sol.} + 48{\cdot}25 \text{ cals.}$$

The comparison of the values of the three isomers shows that the *acidimetric value* measured thermically by *the heat of formation of a solid neutral potash salt*, varies for each of the three isomers :—

Position 1 : 3 ethyl-malonic acid + 48·25 cals.
,, 1 : 4 methyl-succinic acid + 45·18 ,,
,, 1 : 5 normal-glutaric acid + 44·23 ,,

Formation of Furfurol by Cellulose, and its Oxy- and Hydro-derivatives. — Leo Vignon. — The author took equal weights of pure cotton cellulose, and submitted them respectively to the action of (1) acids, (2) oxidising agents, and (3) reducing agents. He obtained three substances; these were left in contact with a cold solution of caustic potash, at 10° B. for five hours; the first and third gave a colourless liquid, the second one a liquid of a pale yellow golden colour; after washing and drying it was found that Nos. 1 and 3 had undergone a loss of weight of 15 per cent, and No. 2 of 25 per cent. Thus oxycellulose is distinctly different from hydro-cellulose, which appears to be identical with hydrogenised cellulose. These were then submitted to the action of boiling hydrochloric acid at 1·06 density, and the furfurol obtained was estimated in the distillate collected, and transformed by phenylhydrazin into hydrazone, according to the following equation :—

$$C_5H_4O_2 + C_6H_5N_2H_3 = C_5H_4ON_2HC_6H_5 + H_2O.$$

Berichte der Deutschen Chemischen Gesellschaft. December 13, 1897.

Organic Derivatives of Selenium.—A. Michaelis and A. Kunckell.—By acting on the ether oxides of naphthol, on the phenols, and the ketones by $SeCl_3$ various compounds are formed. The reactions take place in the cold in ethereal solution; it is fairly energetic. $2CH_3-O.C_{10}H_7 + SeCl_2 = (CH_3O.C_{10}H_6)2Se + 2HCl$; this compound is a reddish crystalline mass, soluble in $CHCl_3$, melting at 138°. The action of $SeCl_2$ on phenol gives a red mass having the formula $Se(C_6H_4.OH)_2$.

Some Organic Derivatives of Tellurium.—E. Rust.—Tetrachloride of tellurium reacts on anisol, giving

$TeCl_2(C_6H_4.OClH_3)_2$, in yellow needles melting at 190°, soluble in ether, benzene, HCl, and the alkalis. The chloroplatinate appears in the form of brown needles, soluble in water and alkalis. The hydrate, bromide, iodide, and nitrate have also been obtained and described. Tetrachloride of tellurium also reacts on phenetol, phenol, and resorcine.

Antimonic Derivatives of Anisol aed Phenetol.—C. Loeloff.—These derivatives are obtained (1) by the action of Na on a mixture of $SbCl_3$ and bromanisol or bromophenetol; (2) by the action of bromanisol on antimoniate of soda. A large number of derivatives are described.

On some Aromatic Compounds containing Bismuth.—A. Gillmeister.—Iodine acts on bismuth-triphenyl in ethereal solution, giving the oxyiodide of bismuth. The iodide, $(C_6H_5)_2BiI$ is obtained by treating an alkaline solution of the chlorine, $(C_6H_5)_3BiCl_2$, by KI. $HgCl_2$ reacts on an alkaline solution of bismuth-triphenyl, giving BiOCl, benzene, and chloromercurate of phenyl. A mixture of nitric and sulphuric acids completely decomposes bismuth-triphenyl into nitrate of bismuth and ortho-dinitrobenzene.

On some Dissymmetric Substituted Phenylhydrazines and their Derivatives.—A. Michaelis.—A certain number of substituted $\alpha\beta$-phenylhydrazines have been prepared by acting on the soda derivative of phenylhydrazine with the alcoholic bromides; the reaction takes place on the water-bath in the presence of benzene. The author describes the hydrochlorate of α-ethyl-phenylhydrazine, ethylindolcarbonic acid, dichlorethyloxindol, dibromethyloxindol, and many other bodies and their derivatives.

Action of Chloroform and Alcoholic Potash on Phenylhydrazine.—S. Ruhemann.—The action of nitric acid on diphenyltetrazoline furnishes two nitrated derivatives, one of which melts above 300° and is difficultly soluble in acetic acid. By reducing it by warm $SnCl_2$ and HCl an amidodiphenyltetrazoline is obtained, crystallising in white needles, fusible at 188°, and soluble in alcohol.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Decolourising Oils.—(Reply to H. Matthews).—Decolourising oils is a rather incorrect expression. There is no process for bleaching rape oils or oils for lubricating purposes; they are rendered paler, but they are not decolourised. This result can be attained by ozone, which at the same time thickens the oil. Dark low-grade fats are transformed into a yellowish material without the use of acid.—EM. ANDREOLI.

Physics of Gases.—Could any of your readers inform me, through your "Notes and Queries" column, if there is any work or works from which I could learn something of the boiling- or liquefying-points of gases (including air), their behaviour under very high pressures, and also their influence or action upon metals. Said works should be as free as possible from technical terms and mathematics. I most particularly desire to know the behaviour under high pressures. Please state prices and publishers.—ENGINEERING STUDENT OF PHYSICS.

ERRATUM.—Vol. lxxvii., p. 263, col 1, line 2 of the paragraph commencing "At the regular meeting," *for* "Breyer and Schweitzer" *read* "Frear and Sweetser."

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Dr. ALEXANDER SCOTT, M.A., D.Sc.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2016.

ON THE

POSITION OF HELIUM, ARGON, AND KRYPTON IN THE SCHEME OF ELEMENTS.*

By Sir WILLIAM CROOKES, F.R.S.

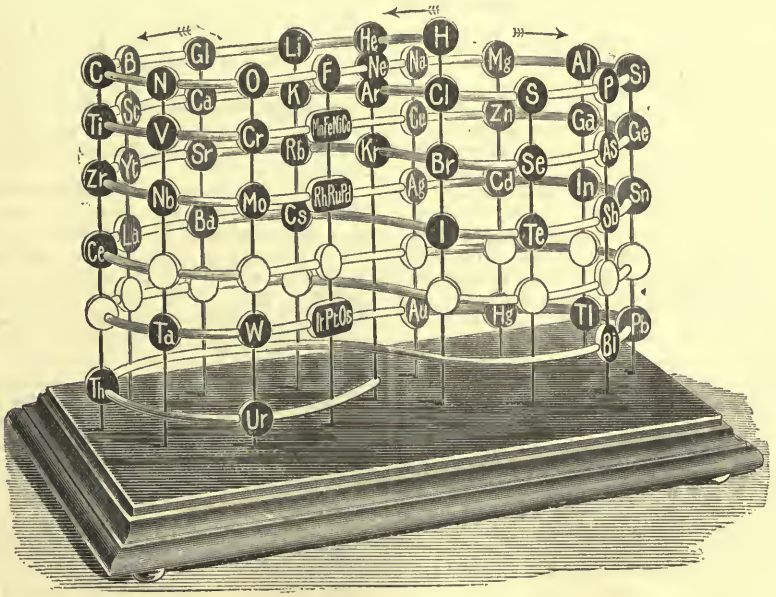
It has been found difficult to give the elements argon and helium (and I think the same difficulty will exist in respect to the gas krypton) their proper place in the scheme of arrangement of the elements which we owe to the ingenuity and scientific acumen of Newlands, Mendeléef, and others. Some years ago, carrying a little further Professor Emerson Reynolds's idea of representing the scheme of elements by a zigzag line, I thought of projecting a scheme in three dimensional space, and exhibited at one of the meetings of the Chemical Society† a model illustrating my views. Since that time, I have re-arranged the positions then assigned to some of the less known elements in accordance with later atomic weight determinations, and thereby made the curve more symmetrical.

Many of the elemental facts can be well explained by supposing the space projection of the scheme of elements to be a spiral. This curve is, however, inadmissible, inasmuch, as the curve has to pass through a point neutral as to electricity and chemical energy twice in each cycle. We must, therefore, adopt some other figure. A figure-of-eight will foreshorten into a zigzag as well as a spiral, and it fulfils every condition of the problem. Such a figure will result from three very simple simultaneous motions. First, an oscillation to and fro (suppose east and west); secondly, an oscillation at right angles to the former (suppose north and south), and thirdly, a motion at right angles to these two (suppose downwards), which, in its simplest form, would be with unvarying velocity.

I take any arbitrary and convenient figure-of-eight, without reference to its exact nature; I divide each of the loops into eight equal parts, and then drop from these points ordinates corresponding to the atomic weights of the first cycle of elements. I have here a model representing this figure projected in space; in it the elements are supposed to follow one another at equal distances along the figure-of-eight spiral, a gap of one division being left at the point of crossing. The vertical height is divided into 240 equal parts on which the atomic weights are plotted, from H = 1 to Ur = 239·59. Each black disc represents an element, and is accurately on a level with its atomic weight on the vertical scale.

The accompanying figure, photographed from the solid model, illustrates the proposed arrangement. The elements falling one under the other along each of the vertical ordinates are shown in the Table.

H	He	Li	Gl	B	C	N	O	F	Na	Mg	Al	Si	P	S
Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn·Fe·Ni·Co	Cu	Zn	Ga	Ge	As	Se
Br	Kr	Rb	Sr	Yt	Zr	Nb	Mo	Rh·Ru·Pd	Ag	Cd	In	Sn	Sb	Te
I	—	Cs	Ba	La	Ce	( )	( )	( )	( )	( )	( )	( )	( )	( )
( )	—	( )	( )	( )	( )	Ta	W	Ir·Pt·Os	Au	Hg	Tl	Pb	Bi	—
—	—	—	—	—	Th	—	Ur	—	—	—	—	—	—	—



The bracketed spaces between cerium and tantalum are probably occupied by elements of the didymium and erbium groups. Their chemical properties are not known with sufficient accuracy to enable their positions to be well defined. They all give coloured absorption spectra and have atomic weights between these limits. Positions marked by a dash (—) are waiting for future discoveries to fill up.

Let me suppose that at the birth of the elements, as we now know them, the action of the *vis generatrix* might be diagrammatically represented by a journey to and fro in

* A Paper read before the Royal Society, June 9, 1898.
† Presidential Address to the Chemical Society, March 28, 1888.

cycles along a figure-of-eight path, while, simultaneously time is flowing on, and some circumstance by which the element-forming cause is conditioned (*e.g.*, temperature) is declining; (variations which I have endeavoured to represent by the downward slope.) The result of the first cycle may be represented in the diagram by supposing that the unknown formative cause has scattered along its journey the groupings now called hydrogen, lithium, glucinum, boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine. But the swing of the pendulum is not arrested at the end of the first round. It still proceeds on its journey, and had the conditions remained constant, the next elementary grouping generated would again be lithium, and the original cycle would eternally reappear, producing again and again the same fourteen elements. But the conditions are not quite the same. Those represented by the two mutually rectangular horizontal components of the motion (say chemical and electrical energy) are not materially modified; that to which the vertical component corresponds has lessened, and so, instead of lithium being repeated by lithium, the groupings which form the commencement of the second cycle are not lithium, but its lineal descendant, potassium.

It is seen that each coil of the lemniscate track crosses the neutral line at lower and lower points. This line is neutral as to electricity, and neutral as to chemical action. Electro-positive elements are generated on the northerly or retreating half of the swing, and electro-negative elements on the southerly or approaching half. Chemical atomicity is governed by distance from the central point of neutrality; monatomic elements being one remove from it, diatomic elements two removes, and so on. Paramagnetic elements congregate to the left of the neutral line, and diamagnetic elements to the right. With few exceptions, all the most metallic elements lie on the north.

Till recently chemists knew no element which had not more or less marked chemical properties, but now by the researches of Lord Rayleigh and Professor Ramsay, we are brought face to face with a group of bodies with apparently no chemical properties, forming an exception to the other chemical elements. I venture to suggest that these elements, helium, argon, and krypton, in this scheme naturally fall into their places as they stand on the neutral line. Helium, with an atomic weight of 4, fits into the neutral position between hydrogen and lithium. Argon with an atomic weight of about 40, as naturally falls into the neutral position between chlorine and potassium. While krypton with an atomic weight of about 80, will find a place between bromine and rubidium.

See how well the analogous elements follow one another in order: C, Ti, and Zr; N and V; Gl, Ca, Sr, and Ba; Li, K, Rb, and Cs; Cl, Br, and I; S, Se, and Te; Mg, Zn, Cd, and Hg; P, As, Sb, and Bi; Al, Ga, In, and Tl. The symmetry of these series shows that we are on the right track. It also shows how many missing elements are waiting for discovery, and it would not now be impossible to emulate the brilliant feat of Mendeléef in the celebrated cases of Eka-silicon and Eka-aluminium. Along the neutral line alone are places for many more bodies, which will probably increase in density and atomic weight until we come to inert bodies in the solid form.

Four groups are seen under one another, each consisting of closely allied elements which Professor Mendeléef has relegated to his 8th family. They congregate round the atomic weight 57, manganese, iron, nickel, and cobalt; round the atomic weight 103, ruthenium, rhodium, and palladium; while lower down round atomic weight 195 are congregated osmium, iridium, and platinum. These groups are interperiodic because their atomic weights exclude them from the small periods into which the other elements fall; and because their chemical relations with some members of the neighbouring groups show that they are interperiodic in the sense of being formed in transition stages.

Note, June 22, 1898.—Since the above was written, Professor Ramsay and Mr. Travers have discovered two other inert gases accompanying argon in the atmosphere. These are called Neon and Metargon. From data supplied me by Professor Ramsay, it is probable that neon has an atomic weight of about 22, which would bring it into the neutral position between fluorine and sodium. Metargon is said to have an atomic weight of about 40; if so, it shares the third neutral position with argon. I have marked the positions of these new elements on the diagram.

SOME OBSERVATIONS ON A PAPER BY MESSRS. DUNSTAN AND HENRY ENTITLED "A CHEMICAL INVESTIGATION OF THE CONSTITUENTS OF INDIAN AND AMERICAN PODOPHYLLUM."

By F. B. POWER, Ph.D., F.C.S.

In a paper published in the *Journal of the Chemical Society*, April, 1898, pp. 209—226, bearing the above-mentioned title, there are some errors and omissions which ought to be corrected. On page 209 the authors make the following statement:—"The chemical constituents of the rhizome of the American Podophyllum peltatum have, however, been made the subject of several investigations. First, in 1832, Hodgson prepared the mixture of resins known and largely used in medicine as 'podophyllin' by precipitating a concentrated alcoholic extract of the rhizome with water; this is now manufactured on a large scale, and is the form in which 'podophyllum' is usually administered as a drug. *The first important contribution to the chemistry of Podophyllum was that made by Podwyssotski* (*Pharm. Journ.* (iii.), 12, pp. 217, 1011). *This chemist showed that the rhizome did not, as was previously supposed, contain the alkaloid berberine.*"

From this statement the inference would naturally be drawn that Podwyssotski was the first to prove the absence of berberine in Podophyllum.

The absence of berberine, or any other alkaloid, in Podophyllum was first conclusively proved and recorded by me in 1877, or four years before the publication of Podwyssotski's first paper on Podophyllum, as may be seen from the following extract from the *Proc. Amer. Pharm. Assoc.*, 1877, p. 425:—"The rhizome of Podophyllum peltatum contains *no* berberine, and the colouring matter is a constituent of the resin itself; a fact all the more surprising when we consider that for a period of nearly half a century the supposed presence of this alkaloid in the rhizome should have become so universally accepted; and from time to time confirmed, without ever having been isolated from it." And again (*loc. cit.*, p. 433), "to briefly summarise the results of these experiments, it may finally be observed that Podophyllum contains no alkaloid, and that the yellow colouring principle heretofore supposed to be due to berberine is due to the resin, and to that portion of it which is of acid character and which may with some degree of propriety receive the previously applied name of podophyllinic acid, which has also in chemical behaviour many analogies to quercitrin."

Podwyssotski, indeed, never claimed to have first shown the absence of berberine in Podophyllum, but simply confirmed my observations that no alkaloid was present. In his chronological review of the investigations preceding his own (see *Pharm. Zeitschrift für Russland*, 1881, p. 888), he refers to a note by Flückiger in the French translation by Lanessan of the first edition of *Pharmaco-*

graphia (*Histoire des Drogues*, 1878, i., p. 90), which is as follows:—"Je ne saurais confirmer la présence de la berberine dans cette racine: je l'en trouve dépourvue.—F.A.F." This note was apparently written at about the time that I was engaged in an investigation of Podophyllum in the laboratory of Professor Flückiger at Strassburg. It is therefore of interest to note what Professor Flückiger has also written on this subject in the *Pharmacographia*, 2nd edition, 1879, p. 38:—"F. F. Mayer, of New York, stated Podophyllum to contain, beside the resin already mentioned, a large proportion of *berberine*, a colourless alkaloid, an odoriferous substance which might be obtained by sublimation in colourless scales, and finally saponin. From all these bodies the resin as prepared by Power was ascertained by him to be destitute; *he especially proved the absence of berberine in Podophyllum.*"

In the "National Dispensatory," 5th edition, 1894, p. 1368, under the title "Resina Podophylli," Professor Maisch has written: "F. B. Power (1877), observed that the largest portion of the resin consists of at least four compounds, differing in their solubility in ether and hot water, and in their behaviour to alkalies, ferric chloride, and lead acetate; fused with potassa *protocatechuic acid was obtained, but no resorcin.*"

And again, under "Podophyllum" (*loc. cit.*, p. 1267), "F. F. Mayer (1863) announced the presence of berberine and another (white) alkaloid, and of saponin, but the investigations of F. B. Power (1877-8) indicate the total *absence of saponin and of any alkaloid*, and we (Professor Maisch) have *subsequently* shown that at all periods of its growth the rhizome is free from alkaloid."

The "United States Dispensatory," 17th edition, p. 1154, states:—"The researches of Power, Maisch, Guareschi, and Podwyssotski have established the fact that Podophyllum does not contain berberine or any alkaloid, and that its activity is due to principles present in the resin."

Also in "Thorpe's Dictionary of Applied Science," 1895, vol. iii., p. 351, under "Podophyllum Resin," we find the following recorded:—"Besides the resin upon which the purgative property of the drug depends, Mayer, who examined Podophyllum in 1863, reported it to contain berberine, saponin, and a colourless alkaloid, but no evidence of these compounds, at least in the crude resin, has been obtained by subsequent observers (Power, *Amer. Journ. Pharm.*, 1878, p. 369; Maisch, *Ibid.*, 1879, p. 590; Biddle, *Pharm. Journ.*, (3), 10, p. 468.)"

"Watts' Dictionary of the Economic Products of India," vi., part 1, p. 301, states under "Podophyllum":—Cadbury, Power, and others affirm that the medicinal virtue is due to the resin soluble in ether, and that the other resin left behind in the alcoholic medium is comparatively inert. The experiments of Power, Maisch, Guareschi, Podwyssotski, and others, prove that Podophyllum does not contain berberine (as was announced by Mayer) or any alkaloid, and that its activity is due to the resin or resins.'

The "Imperial Institute Handbooks of Commercial Products," No. 3, p. 3, under "Podophyllum," reproduces the article from "Watts' Dictionary of Economic Products" as quoted above.

Podwyssotski also did not omit to give credit, for in the *Pharm. Zeitschrift für Russland*, Nov. 1, 1881, No. 44, p. 777, he says:—"Im Anfange der vorleigenden Anhandlung erwähnte ich dass sich mit der Untersuchung des Podophyllins hauptsächlich Buchheim in Deutschland, Power in Amerika, und Guareschi in Italien beschäftigten."

In considering the action of fused potash on podophyllotoxin and on podophylloresin, Messrs. Dunstan and Henry (*loc. cit.*, pp. 216, 222), refer to the investigation of Guareschi, but make no mention of the fact that two years before the publication of Guareschi's paper (*Ber. d. Deutsch. Chem. Ges.*, 1879, p. 683), I had observed and recorded the formation of protocatechuic acid as a product of the action of fused potassium hydroxide on podophyllin (*Proc. Amer. Pharm. Assoc.*, 1877, p. 428), and this point of the investigation was even subsequently extended to ascertain whether protocatechuic acid is a natural constituent of the rhizome of Podophyllum (*Amer. Journ. Pharm.*, 1878, p. 369). By the action of fused potassa on podophyllin it was likewise observed and recorded that volatile acids are formed (*loc. cit.*, p. 428) and by the action of fused potash on Podophyllotoxin, Messrs. Dunstan and Henry have now identified the volatile acid formed as acetic acid.

Although Messrs. Dunstan and Henry may be acceded the privilege of their own opinion in considering the investigation of Podwyssotski to be "the first important contribution to the chemistry of Podophyllum," it is an error to state or to suggest that Podwyssotski was the first to prove "that the rhizome did not, *as was previously supposed*, contain the alkaloid berberine."

It is not desirable at this time to enter into a more extended discussion of the paper by Messrs. Dunstan and Henry, and the interpretation of their results.

AN IMPROVED AND NOVEL FORM OF ACCUMULATOR FOR RAPID AND HEAVY DISCHARGES.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

THIS energetic secondary, which has been specially designed for experimental purposes where high tension is required, differs from all other forms of accumulators which have been from time to time enumerated throughout the pages of scientific literature, not only as regards the construction of the plates, but also as to the non-sulphating nature of the same. The grids in the first instance, previous to pasting, are so turned by suitable appliances that the positive plate after the operation presents a true cylinder, which is further surrounded by its accompanying negative to within one quarter of the total circumference of the positive cylinder.

Within the positive cylinder is now introduced a second small negative plate, insulated from the surrounding positive and attached to the outside negative, the insulations being carefully effected by means of asbestos.

The entire grids are afterwards transformed into true plates by thoroughly incorporating the perforations of the grids with a paste composed of red lead, litharge, and vitriol, in suitable proportions, the plates thus so far constructed being immediately transferred to the air-bath in order to undergo the (second) process of baking. This process requires the greatest skill on the part of the operator, and, if successfully carried out, a plate taken from the oven whilst still hot should present a surface of sufficient hardness to be with difficulty scratched by means of the point of a knife, and show practically no deterioration when suddenly plunged into cold water,—rather a severe test when compared with other forms of plates, but by no means too severe, as extended experience has shown us, when dealing with rapid discharges.

After the plates have withstood the above tests, they are at once removed to the reducing tanks, and thereby brought to the condition of spongy lead by the reducive action afforded by means of amalgamated zinc in contact with dilute sulphuric acid. The plates thus partially formed, after the necessary process of lixiviation has been bestowed upon them, are mounted in cylindrical fashion, as above described, while the true formation of the plates is now accomplished in the usual manner, using a current corresponding to the square surface presented by the plates in the first instance: at the same time the non-sulphation of the plates is effected by the introduction of certain phosphatic compounds in proportion to the quantity of dilute sulphuric acid employed. The cells thus produced are very quickly re-charged, and also admit of very rough usage.

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ON THE YTTRIC EARTHS CONTAINED IN THE MONAZITE SANDS.

By O. BOUDOUARD.

In a previous paper (*Comptes Rendus*, cxxii., p. 697), in collaboration with the late M. Schützenberger, I predicted the possible existence of a new earth precipitable by oxalic acid, not giving an insoluble double sulphate with the alkaline sulphates, and of which the atomic weight should be about 102. This was only a first indication, and it is the results I have since obtained that I now have the honour of presenting to the Academy.

A. I mixed the oxides of which the atomic weights of the corresponding metals were 102·2, 102·45, 102·6, 103, and 102·4, and dissolved them in nitric acid. The nitrate was transformed into sulphate, and, after the addition of sulphate of potassium to remove the earths of the cerium group (*Comptes Rendus*, cxxvi., p. 900), the yttric earths were precipitated with ammonia. The hydrates after being washed, to get rid of all traces of alkali, were dissolved in nitric acid. This nitrate was submitted to fractional fusion at 325°:—

	Atomic weight.
Sub-nitrate	103·0
Mother-liquors	97·7

The oxide 103, transformed into nitrate and submitted to a fresh fusion, gave—

	Atomic weight.
Sub-nitrate	109·5
Mother-liquors	100·6

Finally, the mother-liquor 97·7, by an analogous fractionation, gave—

	Atomic weight.
Sub-nitrate	98·7
Mother-liquors	97·5

B. In this second series I mixed different oxides, the atomic weights of the corresponding metals varying from 95·1 to 99·1 (the greater part gave figures varying from 98·2 to 99·1). I then applied the above-mentioned treatment to this mixture, and the yttria earths thus obtained were dissolved in nitric acid. The nitrate was submitted to a fractional fusion at 325°, which gave—

	Atomic weight.
Sub-nitrate, No. 1 ..	103·6
,, No. 2 ..	97·5
Mother-liquors	96·7

The sub-nitrate No. 1, submitted to a fresh fusion, was divided into two portions:—

	Atomic weight.
Sub-nitrate, No. 1 ..	108·5
Mother-liquors	98·5

C. I then mixed all the oxides of which the atomic weights of the corresponding metals varied from 96 to 112. I collected about 70 grms. of this mixture.

After having eliminated the earths of the ceric group by sulphate of potassium, the unprecipitated oxides were dissolved in nitric acid, and hyposulphite of soda was added to the neutral solution of the nitrate. A precipitate was formed; the reaction is quicker when the solution is warmed than in the cold. The precipitate is collected on a filter and washed. In the clear solution the excess of alkaline hyposulphite is removed, and the unprecipitated earths are brought to the state of oxalates. I thus obtained 45 grms. of earths precipitable by hyposulphite of sodium, and 25 grms. of earths which were not so precipitable. I am now studying these two fractions. This property of hyposulphite of soda seems to me to be so much the more interesting as Fresenius, in his "Traité de Chemie Qualitative" (eighth French edition, p. 134), states that the salts of yttrium are not precipitated by hyposulphite of soda.

The yttric oxides examined in the above three series give almost colourless solutions, of which the absorption spectrum is very feeble; it is characterised by the following wave-lengths:—

657—663	Very faint (erbium)
643—639	,, (holmium)
537	,, (holmium)
524—522	Faint (erbium).

The solutions examined under a thickness of 4 c.m. were saturated; the earth was in the state of sulphate.

If we now compare the results obtained in the first two series, we observe that the minimum atomic weight reached is 96·7, and that the other numbers obtained are in the neighbourhood of 97·5. We are far from the atomic weight of yttrium, which is 89·5.

M. Drossbach (*Berichte*, vol. xxix., No. 15, p. 2452; *Moniteur Quesneville*, May, 1897, p. 351), in examining a monazite, announced the probable existence of an earth with an atomic weight of about 100. He is of the opinion that there is therein a new series of earths in the proportion about 20 to 30 per cent.

MM. Urbain and Budichowski (*Comptes Rendus*, cxxiv., p. 618, and cxxvi., p. 835), in fractionating the acetylacetonates of the yttric earths, and M. Urbain in examining the ethylsulphates, reached a low limit of fractions which could no longer be split up,—a limit which did not go below 95.

These results—later than those of M. Schützenberger and myself, who predicted them—now confirm what we anticipated.

Ought we, from this collection of facts, to conclude that the presence of a new earth is proved? or have we only to deal with a mixture of yttria and of an earth with a higher atomic weight? According to this hypothesis, it is necessary to admit of a mixture of more than 90 parts of yttria to 10 of erbia (average atomic weight 97·6), or of ytterbia (average atomic weight 98·2), or of terbia (average atomic weight 95·7)

Nordenskiöld (*Comptes Rendus*, ciii., p. 795), in 1886, obtained an oxide with a constant atomic weight of 107, which he called *oxide of gadolinium*; he thought that he was authorised to admit that oxide of gadolinium, although not an oxide of a simple body, but a mixture of three isomorphous bodies, even when obtained from minerals altogether different and found in localities very far apart from one another, possesses a constant atomic weight. Is the oxide with the atomic weight 97 an oxide of the same kind?

On the other hand, is it permissible to suppose the existence of a new element very near yttrium? This hypothesis is not untenable; it is sufficient to recall the discussion between M. Lecoq de Boisbaudran and Sir William Crookes (*Comptes Rendus*, cviii., p. 165) on the nature of yttrium.

Sir William Crookes called *yttria* a mixture of earths endowed with varied fluorescence, and of which the elements formed a family of bodies very close together,—species of yttriums, with atomic weights oscillating round about 89; in any case these different yttrias gave the same spark spectra.

M. Lecoq de Boisbaudran called yttria the non-fluorescent earth (which we may suppose to be simple or complex) producing the well-known spectrum, and of which the atomic weight is 89.

To sum up, the process of fractionations (sulphates, nitrates, acetylacetonates, ethyl-sulphates) gives a low limit beyond which no further splitting up takes place; this limit is round about 96.

Is this limit only apparent? This is a point which researches I am now actually engaged on may perhaps elucidate.—*Comptes Rendus*, cxxvi., No. 23, June 6, 1898.

ON THE BOILING-POINT OF LIQUID OZONE.

By L. TROOST.

P. HAUTEFEUILLE and J. CHAPPUIS were the first to obtain ozone in the liquid state, in the year 1882; it was of an indigo-blue colour (*Comptes Rendus*, xciv., p. 1249, 1882).

Some experiments relative to the determination of the boiling-point of this liquid were carried out in the year 1887 by M. Olszewski. This experienced *savant*, after having liquefied the ozone in a tube cooled down to −184·4° by liquid oxygen boiling at the atmospheric pressure found that (*Vien. Monats. fur Chem.*, viii., p. 69, 1887) the ozone only volatilises very slowly when in a tube placed in liquid ethylene cooled down to −140°, but that it volatilises very rapidly when the temperature of the ethylene approaches its boiling-point. From this he concluded that the boiling-point of liquid ozone would be about −106°. I determined to fix this temperature with greater precision. For this estimation I used, as a thermometric apparatus, an iron-constantin couple furnishing a curve given by melting ice, by the boiling-points of chloride of methyl alone, or traversed by a rapid current of air, by the temperature of a mixture of solid carbonic acid and of chloride of methyl (the temperatures were taken in these last two cases by means of a thermometer graduated according to the indications of the hydrogen thermometer), by the boiling-point of protoxide of nitrogen, by that of liquid ethylene, by the melting-point of solid ethylene, and by the boiling-point of liquid oxygen at the atmospheric pressure. By means of this apparatus temperatures could be read to less than half a degree.

The ozone was obtained by using a Berthelot ozoniser, kept at about −79° by a mixture of solid carbonic acid and chioride of methyl. The liquefaction is produced in a vertical tube, the lower part of which is immersed in a bath of liquid oxygen, contained in a cylindrical glass vessel with double sides, with the intermediary space exhausted to a Crookes vacuum, as recommended by Prof. Dewar.

The ozone liquefies before reaching that part of the tube which is immersed in the liquid oxygen, at a point situated about 2 c.m. above the level of the bath, thanks to the low temperature due to the oxygen gas coming off.

The liquefied ozone collects in small drops having an oily appearance and not wetting the glass; they fall to the bottom of the tube, where there had already been placed one of the joints of the iron-constantin couple;* the other was kept in melting ice. To determine the boiling-point of liquid ozone, the bath of liquid oxygen was lowered until its free surface was about 3 c.m. below the lower extremity of the tube holding the liquid ozone, and the successive deviations shown by the Deprez-d'Arsonval galvanometer were noted. The deviation, after having slowly diminished, remains steady during the time that the liquid ozone is in a state of ebullition; it then goes down again very rapidly until the joint of the couple reaches the temperature of the oxygen gas at this point.

The stationary deviation, transferred to the curve, corresponds to a temperature of −119°. I have tried this experiment several times, on different quantities of liquid, and I have always obtained the same result.†

We may therefore conclude that the boiling-point of liquid ozone at the atmospheric pressure is −119°.

The liquid oxygen used in these experiments was obtained by means of an apparatus constructed according to the method given by Prof. Dewar—using commercial compressed oxygen cooled down to −79° in a long serpentine tube. In this manner about a quarter of a litre of liquid oxygen can be obtained in the laboratory or the lecture-room in less than half an hour, without the use of pumps or any motive power.—*Comptes Rendus*, cxxvi., No 25, June 20, 1898.

* An experiment in which one of the joints of the couple, already cooled in liquid oxygen, was lowered into ozone already liquefied and kept at 184·4°, was interrupted by a violent explosion.

† I was helped very considerably in these experiments by one of my old pupils, M. Lamotte, now at the Sorbonne.

A METHOD OF ESTIMATING NITRITES IN WATER.

By LUCIEN ROBIN.

THIS process is based on the fact that when we add pure iodide of potassium to a solution of a nitrite, then a little acetic acid, and let it stand for some time, the quantity of iodine set at liberty is always the same for a given quantity of nitrous acid, if we take care that the conditions of the experiment are always identical. The free iodide is estimated by means of a weak solution of hyposulphite of soda.

The method of working is as follows:—

If the water is not clear, it is necessary to filter it; if it is much coloured, sulphate of alumina and carbonate of soda must be successively added to it, as in the metaphenyldiamine method, in which we measure 100 c.c., to which are added 2 c.c. of glacial acetic acid; we then collect 50 c.c. of this solution by distillation.

Finally, if the water contains sulphuretted hydrogen, we treat 125 c.c. with a solution of sulphate of silver, then—after having filtered 100 c.c.—distil as above.

But in any case we add to 50 c.c. of the water under examination 2 c.c. of a chemically pure solution of iodide of potassium at 20 per cent; then, after shaking well, 2 c.c. of glacial acetic acid; shake again, and allow to stand for exactly half an hour; after having added a small quantity of starch solution, we determine the free iodine by means of a weak solution of pure hyposulphite of soda, prepared by diluting down 50 c.c. of the decinormal solution (24·764 grms. per litre) to 1 litre. We then look in the table below for the quantity of free nitrous acid per litre, according to the quantity of hyposulphite used. If the tint then becomes of a yellowish brown, it is necessary first of all to dilute the original sample of water. On the other hand, it is necessary to make quite sure that the iodide used is quite free from iodate, by making a blank experiment with it.

We can by this means recognise and estimate 0·005 m.grm. of nitrous acid in 50 c.c. of water,—that is to say, 0·1 grm. per litre.

The sensitiveness of this method is very great, and superior to that of the metaphenylene-diamine method. On a large number of experiments that I have made the greatest difference has been 0·3 m.grm. per litre, and that with waters of very diverse characters.

TABLE giving in m.grms. per litre the quantity of nitrous acid contained in a litre of water, according to the number of c.c. of the solution of hyposulphite of soda used, the sample taken being 50 c.c.

Hyposulphite c.c. used.	Nitrous acid per litre.	Hyposulphite c.c. used.	Nitrous acid per litre.	Hyposulphite c.c. used.	Nitrous acid per litre.	Hyposulphite c.c. used.	Nitrous acid per litre.
C.c.	M.grm.	C.c.	M.grm.	C.c.	M.grm.	C.c.	M.grm.
0·4	0·1	7·3	1·1	13·3	2·1	16·4	3·1
0·9	0·2	8·0	1·2	13·7	2·2	16·5	3·2
1·4	0·3	8·8	1·3	14·2	2·3	16·6	3·3
2·1	0·4	9·6	1·4	14·4	2·4	16·8	3·4
2·7	0·5	10·5	1·5	14·9	2·5	17·0	3·5
3·5	0·6	11·1	1·6	15·2	2·6	17·3	3·6
4·3	0·7	11·6	1·7	15·5	2·7	17·4	3·7
4·9	0·8	11·9	1·8	15·8	2·8	17·5	3·8
5·9	0·9	12·2	1·9	16·0	2·9	17·6	3·9
6·6	1·0	12·7	2·0	16·3	3·0	17·7	4·0

The figures in this table have been established by using distilled water to which has been added nitrite of soda in increasing doses, and four estimations made on each sample; I then took the mean.

Note.—If for one reason or another we cannot do the titration with the hyposulphite immediately the half-hour is up, it will be necessary to stop the decomposing action of the acetic acid on the nitrites, and thus the liberation of iodine, by adding 10 c.c. of a concentrated solution of pure carbonate of potassium.—*Journ. de Pharm. et de Chim.*, Series 6, vol. vii., No. 12, June 15, 1898.

ON THE ACTION OF SOME CARBONATES ON CHROMOUS ACETATE.

By G. BAUGÉ.

In a paper entitled "On a Crystallised Ammoniacal Chromous Carbonate," published in the *Comptes Rendus* (vol. cxxii., p. 474), we showed that if an aqueous solution of an alkaline carbonate was treated with chromous acetate, a double carbonate of protoxide of chromium and the alkali was formed; we have since been able to prepare, by the same method, a double carbonate of protoxide of chromium and sodium (*Comptes Rendus*, cxxv., p. 1177.

We have now examined the action of carbonate of potassium, carbonate of magnesium, and the carbonates the alkaline earths on chromous acetate.

Some time ago, M. Henri Sainte-Claire Deville (*Ann. de Chem. et de Phys.*, Series 3, vol. xxxiii., p. 75) pointed out that by reacting with a solution of bicarbonate, sesquicarbonate, or an alkaline neutral carbonate, on a soluble metallic salt, we could prepare double carbonates.

Action of Carbonate of Potassium. — Carbonate of potassium forms two compounds with chromous carbonate, one yellow, the other a reddish brown.

Preparation of the Yellow Salt.—A current of carbonic acid is brought into the tubulated flask of the apparatus already described (*loc. cit.*), then a certain quantity of chromous acetate suspended in water is introduced. After standing, the limpid solution is decanted and replaced by a solution of one-fifth the strength of carbonate of potassium in boiled water. On agitating the chromous acetate is dissolved, and a yellow crystalline powder is then precipitated. The above degree of concentration is important to notice, for in the case of liquids richer in carbonate of potassium the salt is decomposed too slowly, and when the solution is weaker it remains completely dissolved.

After decanting the mother-liquors, we wash the product first with cold boiled water, using as small a quantity as possible, until the wash-waters do not contain any more acetate of potassium; then with alcohol at 98°, and this is continued until the alcohol leaves the apparatus at the same strength at which it enters. After a final decantation the product is dried in the same flask, by placing it over a water-bath containing water boiling freely.

The compound can also be prepared by acting on the moist acetate with a warm saturated solution of bicarbonate of potassium. In this case a strong effervescence takes place, due to the giving off of half the carbonic acid.

Properties. — This salt is a powder having a yellow colour very similar to that of ferrous oxalate. Under the microscope it appears under the form of citron-yellow hexagonal prisms. It is soluble in water, which it colours a yellowish brown.

Solutions thus obtained gradually deposit the salts they contain, and at the same time lose their colour. If we attempt to take up the deposited salt with boiled water, we observe that its solubility is much diminished, and may even become *nil* after a few months.

Independently of this polymerisation, certain agents—and in particular carbonate of potassium—added to the solution of this salt will cause a partial, or even total, precipitation if the addition is sufficient.

Like the corresponding compounds of ammonium and sodium, it is an energetic reducing agent. It decomposes water below the boiling-point. When heated *in vacuo*, or in a current of inert gas, it has the property—like the corresponding yellow salt of sodium—of becoming brown, then regaining its original colour on cooling: this phenomenon takes place up to 280°, at which temperature it decomposes.

Chlorine and sulphuretted hydrogen attack it when warm, giving the same reactions as the yellow salt of sodium.

Though stable for some time in dry air, it quickly oxidises in moist air with the formation of a hydrated sesquioxide of chromium.

Heated in air, it gives the corresponding chromate.

Finally, dilute acids dissolve it when kept from the air, giving blue solutions.

Analysis.—When calcined in a current of dry air, and deprived of carbonic acid, this salt gives us water and carbonic acid. In the chromate of potassium which forms the residue, the chromium was determined in the state of oxide after precipitation by mercurous nitrate; then the potash was estimated in the form of sulphate after eliminating the mercury by means of sulphuretted hydrogen. The following results were obtained:—

	I.	II.	Theory.
CO_2	31·70	31·92	31·76
K	28·01	27·98	28·15
Cr	18·76	18·89	18·77
H_2O	9·70	9·91	9·74

The red salt of which we have already spoken is prepared by placing the yellow salt in boiled water, and passing a current of carbonic acid for a prolonged period. The yellow salt becomes gradually transformed into a brick-red compound. This transformation is also effected in alcohol at 60°. Unfortunately the attack is only superficial, and the product of the reaction has not a constant composition. This red substance can be prepared directly by acting on moist chromous acetate with a 1/30th solution of carbonate of potassium in the exact quantity necessary. In this case a red precipitate is formed which is partially destroyed by washing, and of which the analysis could not be made.

This salt, like the preceding one, decomposes water at 100°.

Action of Carbonate of Magnesium.—If we place a moist solution of chromous acetate in contact with a saturated solution of hydrocarbonate of magnesium, in water charged with carbonic acid, a reaction takes place with the formation of a brownish red body which decomposes water on boiling. We have not been able to make the analysis, for at the same time that the double salt is precipitated there is a deposit of carbonate of magnesium, which we have not been able to separate in a satisfactory manner.

We have not succeeded in obtaining double compounds with the alkaline earthy carbonates.

To sum up, chromous carbonate forms with carbonate of potassium a double salt of a yellow colour, in sharp well-defined crystals, to which analysis gives the formula $(CO_3K_2,CO_3Cr)_2 3H_2O$, and a crystallised double salt of a reddish colour with an undetermined formula. Carbonate of magnesium combines with chromous carbonate, giving a reddish brown compound.

The alkaline earthy carbonates are without action.—*Comptes Rendus*, cxxvi., No. 22, May 31, 1898.

SOLUTIONS OF SILICATES OF THE ALKALIES.*

By LOUIS KAHLENBERG and AZARIAH T. LINCOLN.

Introduction.

THE electrical conductivity of solutions of sodium silicates has been investigated by F. Kohlrausch (*Zeit. Phys. Chem.*, xii., 773, 1893), who worked mainly with the compounds corresponding to the formulæ Na_2SiO_3 and $Na_2O.3.4SiO_2$, although he also tested the conductivity of solutions containing sodium hydroxide and silicic acid in other proportions varying from pure NaOH to the acid silicate just mentioned. Kohlrausch obtained the solution of the normal silicate by dissolving the crystallised salt ($Na_2SiO_3 + 9H_2O$) in water, while that of the acid silicate was prepared by boiling the solution of the normal salt with excess of silicic acid. By mixing sodium hydroxide with various quantities of the acid silicate, the other solutions mentioned were obtained. Kohlrausch found that a dilute solution of sodium silicate conducts electricity better than that of any other salt of equivalent concentration, and concludes that this is due to the fact that in solution this salt suffers hydrolytic decomposition into sodium hydroxide and silicic acid. In concentrated solutions Na_2SiO_3 was found to be a rather poor conductor. Dilute solutions of the acid silicate were also found to conduct well, while strong solutions showed an abnormally low conductivity. This behaviour is also explained by the hydrolytic decomposition of the salt. Kohlrausch (see paragraph 2, p. 773; also p. 778, *loc. cit.*), appears to give this explanation in rather a tentative way, for, besides the fact that silicate solutions have an alkaline reaction and that the alkali they contain can be estimated by titrating with a normal acid, he had simply the results of conductivity determinations upon which to base his argument. No doubt the high conductivity of a solution of Na_2SiO_3, which, if the salt were supposed to dissociate into the ions 2Na and SiO_3, would necessitate the assumption that the latter ion has a mobility exceeding that of the chlorine ion by about 70 per cent, is an excellent reason for believing that the silicate is decomposed into NaOH and silicic acid, and that the great conductivity of the solution is due to the presence of the mobile ion OH; nevertheless a determination of the freezing-points of solutions of silicates together with conductivity investigations, would more definitely answer the question as to whether these compounds are hydrolytically decomposed, and would furthermore enable one to make a quantitative estimate of the extent of such decomposition. To determine the extent of the hydrolytic decomposition of the silicate from the electrical conductivity of its solution is not possible, for the silicic acid split off exercises an unknown retarding influence on the movements of the ions. It is possible only to state, as Kohlrausch does, that in very dilute solutions the decomposition is very great and that probably even in strong solutions it is still appreciable. Colloidal silicic acid has but very little effect on the freezing point, as is well known; indeed, in the case of a solution of sodium silicate the lowering of the freezing-point caused by the colloidal silicic acid present is generally so small that for most purposes it may be left out of consideration. From this it is evident that from the lowering of the freezing-point of a silicate solution the extent of the hydrolytic decomposition of the salt may be calculated very approximately. The present investigation was undertaken in order to throw more light on the nature of silicates in solution; for this purpose the freezing-points and the electrical conductivity of solutions of various silicates were determined.

Experimental Part.

The solutions that were investigated are those of the silicates of sodium, potassium, lithium, rubidium, and cæsium. These solutions were in all cases prepared by adding to a solution of silicic acid, obtained by dialysis according to the well-known method of Graham (*Phil. Trans. Roy. Soc.*, London, 1861), the required amount of a standard solution of the pure hydroxide of the alkali metal. That a solution of sodium silicate thus prepared is the same as that obtained by dissolving the salt will be shown below. It is a well established fact that a solution of NaCl is the same as that obtained by mixing equivalent quantities of NaOH and HCl (*Ostwald, Zeit. Phys. Chem.*, 2, 80, 1888), and consequently it seemed at first unnecessary to prove that a solution of Na_2SiO_3 is the same as a solution of equivalent amounts of silicate acid and caustic soda; but because in the case of silicate solutions equilibrium is established only after a measurable period of time (*Kohlrausch, loc. cit*, p. 783), and because objections might possibly arise to using a colloidal solution of silicic acid in the preparation of silicate solutions and then finding that the latter contain colloidal silicic acid, it was thought best not to omit the experimental proof.

Dialysed solutions of silicic acid were prepared, using crystallised $Na_2SiO_3 + 9H_2O$ and also commercial solutions of water-glass from different manufacturers. In each case the dialysis was carried on until no more chlorides were present in the solutions. No difference was found in the behaviour of the solutions of the silicates prepared from the various colloidal silicic acid solutions thus obtained. The strength of the silicic acid solutions was determined by evaporating a measured quantity to dryness, igniting and weighing the SiO_2; the purity of the latter was always established by finally volatilising the same with hydrofluoric acid—no residue remained.

The solutions of the hydroxides of sodium and potassium were obtained by allowing the metals to act upon water freed from carbon dioxide. The hydroxides of lithium, rubidium, and cæsium were prepared by treating the sulphates of these metals with equivalent amounts of barium hydroxide. The strength of the solutions of these alkaline hydroxides was determined by comparison with a carefully standardised solution of hydrochloric acid.

The freezing-point determinations were made with the apparatus of Beckmann. The thermometer was graduated to hundredths of a degree and admitted of judging the thousandths by use of a lens. The usual precautions (see Ostwald's "Hand. u. Hilfsbuch." in making the freezing-point determinations were carefully observed.

The electrical conductivity was measured according to the method of Kohlrausch. In preparing the various solutions, water carefully freed from carbon dioxide and ammonium salts was used. The water was first distilled from potassium bichromate plus sulphuric acid and then re-distilled from barium hydroxide. A condenser of block tin was used; this was found to yield satisfactory results. The water thus obtained was carefully protected from the carbon dioxide of the air, and special precautions were taken in carrying out all the experiments to exclude the influence of carbon dioxide.

In preparing the silicate solutions the aim was to get fairly strong solutions with which to begin. In attempting this by the method of mixing caustic alkali with colloidal silicic acid some difficulty was encountered. The advantage of using this method of getting the solutions of the various silicates is clearly that, by means of it, it is possible to more conveniently get the alkali and the silicic acid into solution in any desired proportions. The disadvantage is that very strong solutions cannot be thus prepared, for the reason that, when strong solutions of caustic alkali and silicic acid are mixed, the latter gelatinises. Various attempts to get a solution of the normal silicates of sodium or potassium stronger than one-eighth of a grm.-molecule per litre failed because the solutions gelatinised before the proper amount of alkali had been added. Still more difficulty was encountered in preparing the solution of the normal silicate of lithium. In this case a solution containing one thirty-second of a

* *Journal of Physical Chemistry*, vol. ii., No. 2, February, p. 77 (1898).

grm.-molecule per litre was the strongest that could readily be obtained. In mixing the alkali with the silicic acid solution, it was found best to add the former to the latter gradually, always shaking the mixture and waiting until the precipitate that forms temporarily is completely dissolved before adding more alkali. It is best also to heat the silicic acid solution while the alkali is being added. The colloidal solution of silicic acid was slightly opalescent in appearance; the solutions of the silicates, however, were invariably perfectly clear.

Tables I. to IX. give the results of the cryoscopic determinations. In the first column, under *v.* is given the volume in litres in which one grm.-molecule of the salt expressed by the formula is contained. The second column gives the observed lowering of the freezing-point. In the third column are the molecular weights calculated on the supposition that the salt when in solution has the composition indicated by the formula. The fourth column gives the molecular weights calculated on the supposition that there is in the solution only the alkaline hydroxide; that is to say, in this calculation no account was taken of the silicic acid present. The solution of silicic acid that was used in preparing the silicate solutions according to the method above described contained 12·2180 grms. SiO_2 per litre and had a freezing-point of −0·018, which corresponds to the molecular weight 1019.

The first part of Table I. gives the results obtained from freezing solutions of Na_2SiO_3 prepared by mixing solutions of silicic acid with caustic soda as above described; the second part gives the results obtained from freezing solutions of Na_2SiO_3 prepared by dissolving the salt obtained by fusing the alkali and the acid together. It will be observed that the freezing-points of the corresponding dilutions agree fairly well, and justify the conclusion that the solutions are identical. The fact that the depressions in the second series are not quite as large as those in the first, is very likely due to the slight formation of carbonates in case of the salt obtained by fusion, for in the process of fusing it is especially difficult to exclude the influence of carbon dioxide. Tests of the electrical conductivity of the solutions obtained in these two different ways also pointed to the fact that they are identical. The salt obtained by fusion of course had a slightly lower conductivity for the same reason that its solution possessed a slightly higher freezing-point.

Table I. shows that the molecular weights calculated on the assumption that the substance in solution has the formula Na_2SiO_3 approach as their limit the value of one-fourth the calculated molecular weight of Na_2SiO_3. There are then in the dilute solutions four part-molecules active in lowering the freezing-point. The action of water on the silicate may be expressed by the equation—

$$Na_2SiO_3 + \text{water} = 2\overset{+}{Na}, \overset{-}{OH} + \text{colloidal silicic acid.}$$

The four part-molecules that are active in lowering the freezing-points are thus two sodium ions and two hydroxyl ions. As stated above, the effect of the colloidal silicic acid on the freezing-point can—at least for the more dilute solutions investigated—be considered too small to take into account. The results show that this hydrolytic decomposition is nearly complete for the concentration $v=48$, and that it has progressed to the extent of 64·8 per cent* even when $v=8$. The last column of the table giving the molecular weights calculated on the assumption that there is only NaOH in the solution, confirms in a striking manner what has just been said. These results approach as their limiting value one-half the molecular weight of NaOH. This is what would be expected, since this compound dissociates into the ions Na and OH.

The investigations of solutions containing $NaHSiO_3$ yielded the results in Table II. Here the molecular weights calculated from the observed lowerings on the

* This calculation, as well as the similar ones that follow, has been made on the supposition that the caustic alkali present in the solution has suffered practically complete electrolytic dissociation.

Table I.

Na_2SiO_3. Molecular Weight = 121·58.

v.	Freezing-point.	Mol. wt.	Mol. wt. (NaOH).
8	0·695	41·3	27·0
12	0·498	38·4	25·2
16	0·385	37·3	24·4
24	0·280	34·2	23·9
32	0·210	34·9	22·4
48	0·150	31·9	20·9
64	0·110	32·6	21·4

¼ of 121·58=30·39. ½ Mol. wt. NaOH=19·88.

Na_2SiO_3 (obtained by Fusion).

v.	Freezing-point.	Mol. wt.
32	0·200	36·5
48	0·140	34·8
64	0·108	33·8
96	0·077	31·6

Table II.

$NaHSiO_3$. Molecular Weight = 99·7.

v.	Freezing-point.	Mol. wt.	Mol. wt. (NaOH).
8	0·332	70·9	31·0
12	0·263	59·7	26·1
16	0·202	58·3	25·5
24	0·146	53·7	23·5
32	0·110	53·5	23·4

½ of 99·7=49·85.

Table III.

$Na_2Si_5O_{11}$. Molecular Weight = 361·34.

v.	Freezing-point.	Mol. wt.	Mol. wt. (NaOH).
32	0·178	119·9	27·0
48	0·139	102·4	23·1
64	0·104	100·3	22·6
96	0·089	79·9	18·0
128	0·059	90·4	20·4

¼ of 361·34=90·33.

Table IV.

K_2SiO_3. Molecular Weight = 153·46.

v.	Freezing-point.	Mol. wt.	Mol. wt. (KOH).
8	0·710	51·1	37·1
12	0·503	48·1	34·9
16	0·394	45·4	32·9
24	0·279	43·5	31·4
32	0·215	42·2	30·6
48	0·146	41·4	30·0
64	0·110	41·2	29·9
96	0·082	36·8	26·7

¼ of 153·46=38·36. ½ Mol. wt. KOH=27·85.

Table V.

$KHSiO_3$. Molecular Weight = 115·64.

v.	Freezing-point.	Mol. wt.	Mol. wt. (KOH).
8	0·326	83·8	40·4
12	0·248	73·4	35·4
16	0·196	69·7	33·6
24	0·153	59·5	28·7
32	0·110	62·1	29·9
48	0·078	58·4	28·1

½ of 115·64=57·82.

Table VI.

Li_2SiO_3. Molecular Weight = 89·76.

v.	Freezing-point.	Mol. wt.	Mol. wt. (LiOH).
32	0·228	23·3	12·4
48	0·166	21·2	11·3
64	0·120	22·1	10·4
96	0·090	19·6	10·4
128	0·071	18·5	9·9

¼ of 89·76=22·88. ½ Mol. wt. LiOH=11·92.

assumption that the dissolved substance is $NaHSiO_3$ give values that approach as their limit one-half of the molecular weight of $NaHSiO_3$. This shows that in the dilute solutions there are two part-molecules active in lowering the freeeing-point; these are sodium and hydroxyl ions as before. The equation expressing the action of water on $NaHSiO_3$ may be written—

$$NaHSiO_3 + \text{water} = \overset{+}{Na}, \overset{-}{OH} + \text{colloidal silicic acid.}$$

This decomposition is nearly complete at the same concentration as that of Na_2SiO_3, and even when $v=8$ it has progressed to the extent of 40·7 per cent. As in the case of Table I., the values in the last column (obtained on the supposition that the solution is simply one of NaOH) approach the limit of one-half the molecular weight of NaOH.

Table III. gives the results obtained by freezing solutions of the more acid silicate $Na_2Si_5O_{11}$. This salt was selected because a lithium silicate of analogous formula occurs in Nature. The molecular weights in the third column approach as a limit the value of one-fourth the molecular weight of $Na_2Si_5O_{11}$.* Here again then there are four part-molecules active in lowering the freezing-point. The equation—

$$Na_2Si_5O_{11} + \text{water} = 2\overset{+}{Na}, \overset{-}{OH} + \text{colloidal silicic acid}$$

expresses the hydrolytic decomposition that takes place. This decomposition is practically complete at $v=128$, and has gone on to the extent of 67·3 per cent even when $v=32$. In the fourth column the molecular weights, calculated on the basis that there is only NaOH in solution, again approach as a limit the value of one-half of the molecular weight of NaOH. This salt then behaves very much like those of Tables I. and II., except that the hydrolytic decomposition is not as far advanced at the same stage of dilution. This is to be expected from the law of mass action. For a like reason $NaHSiO_3$ is not quite as far dissociated hydrolytically at the same degree of dilution as Na_2SiO_3, though here the difference is less since the amount of silicic acid present has only been doubled, while in the salt $Na_2Si_5O_{11}$ there is five times as much acid (to the same amount of sodium) as is contained in the normal salt.

Tables IV. and V. show the behaviour of solutions of K_2SiO_3 and $KHSiO_3$ respectively. What has been said of the sodium compounds applies also to these salts. The action of water on these silicates may be expressed by analogous equations. At $v=8$ the normal salt is dissociated 66·9 per cent and the acid salt 39 per cent. In both cases the dissociation is practically complete at $v=48$.

(To be continued).

NOTICES OF BOOKS.

A Laboratory Guide in Qualitative Chemical Analysis. By HORACE L. WELLS, Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1898. Pp. vii.—189. 8vo.

A Short Course in Inorganic Qualitative Analysis. (For Engineering Students). By J. S. C. WELLS, Instructor in Analytical Chemistry, Columbia University. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1898. Pp. vii.—294. 12mo.

THESE two works covering practically the same field, published simultaneously by a well-known New York firm, and written by teachers of experience in universities less than 75 miles apart, are quite unlike as respects the methods of treatment and their educational influence. Both admit the value of the classical work of Fresenius and recommend it for reference. Dr. Wells, of Columbia University, follows conservative methods of instruction; Professor Wells, of Yale University, adopts a novel plan for training students to think for themselves. In many ways the two books present marked contrasts; Professor Wells deprecates the use of "tables or abbreviated schemes of analysis," Dr. Wells depends largely on "Schemes," neatly printed on folding sheets for imparting instruction; Professor Wells takes up the study of the groups of radicals (metals) in an inverse order to that followed by Dr. Wells; the former teacher assumes that the students beginning the subject of qualitative analysis possess a good knowledge of elementary chemistry including the fundamental theories; the latter teacher finds it expedient to insert in his book brief paragraphs of descriptive chemistry containing elementary data. Dr. Wells obliges the student to spend much time in examining the individual reactions of the metals and acids, before considering their group relations; Professor Wells introduces the student at once to the behaviour of groups of metals having common reactions. Dr. Wells's method of instruction is adapted rather to drilling large classes of students. Professor Wells, on the other hand, aims to prevent mere mechanical work on the part of the students, and the use of his book pre-supposes close contact with the individual. In both books the subject-matter is clearly and ably presented, and it would be invidious to say that one was decidedly better than the other. A student working through either the "Guide" or the "Short Course" conscientiously, would acquire a good knowledge of qualitative analysis.

Professor Wells places before the beginner twenty-seven solutions in labelled bottles and by studying these with the standard reagents he is expected to become familiar with the behaviour of the metals singly and in groups. The solutions comprise salts of aluminium, ammonium, antimony, arsenic, barium, and so on, to strontium and zinc, all arranged alphabetically. The first exercise is to "find by experiment which of the twenty-seven solutions give precipitates when a few drops of HCl are added to 1 or 2 c.c. in a test tube." The student is then directed to write the equation of each reaction and to remember the facts observed. By this means he becomes acquainted with the Ag, Pb, Hg group. In a similar way the student is directed to make experiments which teach him the methods of recognising the three chlorides when mixed. Results of experiments are never given to the worker with test tube, who is supposed to observe, remember, and reflect. Instructions for ascertaining which of the twenty-seven solutions react with hydrogen sulphide then lead to an acquaintance with a second group, and so on. Part II. is devoted to "Theory," explaining chemical radicals, ionisation and ions, classification of radicals and salts and methods of writing chemical equations. Part III., "Descriptive Part," gives a brief account of the principle reactions of the inorganic radicals and serves as a vocabulary to a reading book in some foreign language. In this part there are constant references to Fresenius. In an appendix are printed in large type labels for the twenty-seven experimental solutions and for reagents both liquid and solid. The pages of labels are perforated to permit their being torn out without injury to the book. A full table of contents serves for an index. The author acknowledged the assistance of Miss L. P. Bush in proof-reading, but both of them overlooked a typographical error in the title on page 1, where qualitative appears as oualitative.

Dr. Wells's "Short Course" follows more closely the lines of Fresenius; the more important reactions of the different metals and acids are first explained, and the separation methods are given in schemes accompanied by notes, and in tables of schemes showing the reactions. These tables of schemes are an important feature of the

* The small molecular weight found corresponding to the concentration $v=96$ is no doubt due to experimental error.

book for those students who take kindly to synoptical diagrams.

Neither of these works teach the student much of blowpipe analysis, as the subject is probably handled in another department or in another treatise, but the writer feels that it is of great advantage to unite the dry and wet methods in elementary instruction, the former often furnishing a quick and accurate means of recognising a substance.

Review and Bibliography of the Metallic Carbides. By J. A. Mathews. Smithsonian Miscellaneous Collections, No. 1090. City of Washington. 1898. 32 pp. 8vo.

Since the manufacture of acetylene gas from calcium carbide has become commercially profitable, the metallic Carbides have acquired new interest, and Mr. Mathews's "Review and Bibliography" will be welcomed by chemists and by firms engaged in industries in which these chemical compounds are used. The compiler's plan is a very good one; he gives a condensed account of the carbides in alphabetical order, and each is followed by references to literature bearing thereon. Moissan leads all other chemists in the number and importance of his contributions to the subject.

Mr. Mathews, writing in 1897, does not speak very hopefully of the future of acetylene gas for the purposes of illumination. In a postscript he gives the literature down to March, 1898. The booklet is published by the Smithsonian Institution on recommendation of the Committee on Indexing Chemical Literature appointed in 1882 by the American Association for the Advancement of Science. H. C. B.

CORRESPONDENCE.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—I fear Mr. Richmond must be left to struggle with "the inadequacy of language to express ideas," since life is too short to follow him in his rambles through the dictionary. But to assist his ideas I will re-state the case as simply as possible.

Cavendish proved that when oxygen, nitrogen, and carbonic acid have been removed from air, a residue remains of unknown composition.

Lord Rayleigh proved that this residue is denser than nitrogen. Wishing to know a little more about the matter, and learning from Professor Dewar what it was that he had done, Lord Rayleigh was proceeding to collect a quantity of this residual gas for experiment when Professor Ramsay appeared upon the scene as a rival collector, and associated himself. Thenceforward the investigation was carried on by the two men jointly, and after a certain time they informed the world that the Cavendish residue is a hitherto unnoticed element, to which they gave the name of argon.

The world was very pleased, and then a little sceptical. The discoverers could not find that their element had a single chemical affinity, and its spectrum was a little peculiar. But they fought for it manfully, explained away its spectroscopic oddities, determined its constants, and all that sort of thing, and finally got the world to acquiesce—perhaps rather languidly—in their discovery.

Things were in this comparatively happy state when argon was suddenly dethroned, and by Professor Ramsay himself. He announced that what had been called argon and an element is two things, one of which he calls krypton, while the other may conveniently retain the original name. Some people were delighted, while others shrugged their shoulders, said they had expected it, and wondered when finality was to be reached. Sure enough the little stranger had scarcely got through its christening when it and argon were further split up to make four new elements by a fissiparous division better known in physiology than in physics. Neon and metargon are the two newest claimants for a place in Mendeleeff's table, but, like argon and krypton, they are known only as the unknown cause of certain lines in the spectrum.

It is a curious thing that, when neon and metargon were discovered, krypton modestly retired into its crypt. The quantity of "argon"—*i.e.*, of Cavendish residue—operated upon represented about the same quantity of air as that employed when krypton was found; yet there was no krypton, and the explanation of its absence did no particular credit to Professor Ramsay's ingenuity. Again, the spectrum which is the sole proof of the existence of metargon can unfortunately be produced by carbonic acid and cyanogen. Still more singular, the characteristic line which proves neon in London, proves metargon in Paris; and that same line D_5, as pointed out last week by "Puzzled," is indifferently produced by a gas having a density of 14·67 and by one of the density 19·87. If neon be spectroscopically equal to metargon, and metargon be equal to carbon compounds, and we don't know anything whatever about either of them except spectroscopically, and if a difference of density of 35 per cent does n't matter a pin, and if neither is found in the common matrix when krypton is discovered, and if krypton vanishes when they are discovered, then, Sir, I want to know—where are we?

I shall be pleased at any time to discuss the ethical standpoint of a gentleman who has posed in *Nature* as an expert on scientific morality. But just at present it is his science, not his morality, that is in question, and our poor language is surely not so hopelessly inadequate as to compel Mr. Richmond to mix up things so distinct. My point is that these unintelligible and contradictory results are not Science, but mere fumbling with Science; and that all we know at this moment about the Cavendish residue beyond what Cavendish knew, is that it is heavier than nitrogen, and is probably a mixture of unknown substances in unknown proportions. Not one of these substances so hurriedly announced by Professor Ramsay has been truly isolated or identified, or scientifically demonstrated in any way. That there are lines in the spectrum of air which do not belong to any demonstrated or accepted element was pointed out by other observers before Professor Ramsay. Will Mr. Richmond kindly point out what is the net addition to precise and positive knowledge that accrues to the world from this extraordinary jumble of argon, krypton, neon, and metargon?—I am, &c.,

Suum Cuique.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 20, May 16, 1898.

Some Causes of Uncertainty in the Exact Estimation of Small Quantities of Carbonic Acid and Moisture in Large Volumes of Air or of Inert Gases.—A. Gautier.—A long paper, not suitable for abstraction.

Liquefaction of Hydrogen and Helium.—J. Dewar.—Already noticed.

On a Crookes Tube Regenerable by Osmose.—P. Villard.—To overcome the principal defects of a Crookes tube when employed for the production of X rays, viz., the

increase or decrease of resistance, the author proposes the addition of a platinum tube closed at one end and with the open end sealed to a glass tube, itself sealed to the bulb. If, now, the platinum tube is heated by means of a Bunsen burner the conditions suggested by MM. Ste.-Claire Deville and Troost are realised. The hydrogen of the flame penetrates the platinum by osmose in a nearly pure state, and thus reaches the interior of the apparatus. The introduction of gas ceases as soon as the flame is withdrawn. If, now, the platinum tube is covered with a platinum sheath, so that the flame does not come in contact with it, but allowing free circulation of the air, and is then heated afresh, the gas previously introduced will now leave the apparatus, still by osmose, and a more perfect vacuum can be thus established. These two operations may be repeated as often as is desired.

On a Property of Fluorescent Screens.—P. Villard.—If a body opaque to X rays be placed between a Crookes tube and a platinocyanide of barium screen, so that the shadow of the obstacle is visible, it will be noticed that when the obstacle is removed and the X rays are allowed to fall on the whole surface of the screen, that part which was previously dark will now appear brighter than the rest; the difference being the more marked in proportion as the obstacle was more opaque.

Atomic Weights of Easily Liquefied Gases.—D. Berthelot.—A mathematical paper, not suitable for abstraction.

Preparation and Properties of Anhydrous Fluoride of Glucinum and of Oxyfluoride of Glucinum.—P. Lebeau.—This paper has already been inserted in full.

Synthetic Method of Forming Carbonylferrocyanide of Potassium.—J. A. Muller.—The author has recently succeeded in forming carbonylferrocyanide of potassium in a very simple manner by heating a solution of ordinary prussiate of potash in an atmosphere of carbonic oxide. If a solution of ferrocyanide of potassium at 200 grms. per litre is left in a closed vessel at the ordinary temperature (15° to 20°) in the presence of a quantity of carbonic oxide, a little more than equi-molecular, after the lapse of twelve hours no appreciable trace of carbonylferrocyanide is formed. After thirty days, $\frac{1}{4}$ per cent of the prussiate used is transformed into carbonylferrocyanide. At 60—65°, the quantity formed is 4 per cent in the same time; at 100° it is greater, and the reaction is much more rapid; and at 130°, it is more than 90 per cent. The reaction is complete in forty-eight hours. Ammonia and formate of potassium are also formed. The reaction may be expressed as follows:—

$$K_4\overline{FeCN_6} + CO + 2H_2O = K_3\overline{FeCN_3CO} + NH_3 + HCO_2K.$$

New Incomplete Tertiary Alcohol, Dimethylheptenol.—Ph. Barbier.—The new unsaturated tertiary alcohol described in this paper is derived from lemonol by the action of alcoholic potash. A mixture of 200 grms. of lemonol and 100 grms. of potash dissolved in a very little alcohol is heated for eight hours at 150°. It is then precipitated by water, and the oily layer which separates is washed with a dilute solution of acetic acid, then with water, after which it is dried. The liquid obtained after two rectifications *in vacuo* gives a substance boiling at 79° at 10 m.m. It gives on analysis:—

	Found.	Calculated for $C_9H_{18}O$.
C	76·08	76·06
H	12·60	12·68

It is a colourless mobile liquid, with an odour recalling that of natural methylheptenone. It fixes one molecule of bromine, and when heated to 140° with acetic anhydride and a little melted acetate of sodium it gives an acetic ether boiling at 84—86° at 11 m.m. This liquid has an agreeable aromatic odour. The substance obtained under the above-mentioned conditions is, therefore, a non-saturated alcohol of the formula $C_9H_{18}O$, differing from the parent alcohol by having one atom of carbon less. The author has determined its constitution by the study of its products of oxidation.

Ethane-pyrocatechin and its Derivatives.—Ch. Moureu.—Ethane-pyrocatechin has already been prepared by Vorlander by heating pyrocatechin with potash, bromide of ethylene, and a little water at 100° in sealed tubes. The author has easily prepared large quantities by heating the mixture in a large flask filled with hydrogen and fitted with a vertical condenser. The product is an oil, insoluble in water, distilling at 216°, with a density of 1·186 at 0°. Permanganate of potash hardly attacks it. Chromic acid in acetic solution completely destroys the molecule, with the formation of oxalic and carbonic acids, without it being possible to isolate any intermediate body of a neutral, quinonic, or acid nature. Ethane-pyrocatechin behaves like an ordinary di-alcoholic ether of orthodiphenol, and the influence on the aromatic nucleus of the ethylenic ether function, which forms the oxygenated nucleus in itself, is analogous to that of two ether oxide functions with the chain open.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 6.

On some Phenomena of Transposition, produced by Means of Hydriodic Acid at a high Temperature.—G. Blanc.—Hydriodic acid is a very powerful reducing agent, frequently used in the transformation of ketones, alcohols, amines, &c., &c. But it has other stronger properties, cited by the author; for instance, when fuming hydriodic acid is heated up to 200° in sealed tubes in the presence of carbide derivatives of the halogens, one obtains, not only the corresponding carbide, but also another product of molecular transposition. In some few cases the second is the only one present in the products of the reaction.

Combinations of Chromic and Titanic Acids.—M. Blondel.—Concentrated chromic acid will dissolve titanic acid. Under the most favourable conditions one equivalent of chromic will dissolve one equivalent of titanic acid. Such a solution is decomposed by progressive dilution, which precipitates products more and more rich in titanic acid. The compound richest in chromic acid is obtained in the state of an ammoniacal salt; the solution of one equivalent of titanic acid in four equivalents of CrO_3 and one equivalent of ammonia gives a precipitate of $2TiO_2,CrO_3,2H_2O$, while the mother liquor, evaporated in vacuo, deposits the salt $TiO_2,3CrO_3(NH_4)_2O,H_2O$ in hexagonal prisms.

On the Separation of the Oxides of Cerium and Thorium.—G. Wyrouboff and A. Verneuil.—Already inserted.

On the Yttric Earths Contained in the Monazite Sands.—P. Schutzenberger and O. Boudouard.—This article has already been inserted in full.

The Synthesis of Xanthic and Allied Bodies starting with Hydrocyanic Acid.—A. Gautier.—A short controversial article in which the author claims priority.

Action of Ammonia on Dithioacetylacetone.—V. Vaillant.—When a current of dry ammonia gas is passed through a solution of dithioacetylacetone in absolute ether at the ordinary temperature a voluminous pale yellow precipitate is obtained. This compound can also be obtained by treating an etherised solution of dithioacetylacetone by ammoniacal alcohol; the precipitate thus prepared is entirely crystalline, and is also much more stable than that obtained by the former method. The precipitate, after rapid filtration and washing with ether, is unstable, and at the ordinary temperature when exposed to air gives off ammonia, and returns to its previous state of dithioacetylacetone, but it can be kept for a long time in its original mother-liquor. The author has tried the same reaction on other compounds, with interesting results.

Thermic Study of the Acid Function of three Oxybenzoic Acids. Influence of Phenolic Oxyhydrile.—G. Massol.—The study of certain figures given by MM. Berthelot and Werner (*Ann. Chim. Phys.*, 6, vol. vii., pp. 146, 148, and 167) appears to show that the phenol function does not appear to exist in salicylic acid, while it is shown very clearly in the case of the meta- and para-isomers. The author decided to study the heat of formation of the three soda salts taken in the solid state. The influence of phenolic oxyhydrile notably stimulated the acid function of benzoic acid, and to determine the influence of alcoholic oxyhydride he took the heat of formation of meta- and para-oxybenzoates of soda. These results differed completely from those found when the acid was neutralised by the base in a weak solution.

The Separation and Estimation of Iodine, Bromine, and Chlorine.—Ad. Carnot.—Already inserted.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Aniline Colours.—Where may I be able to find anything about the colouring power of the several aniline colours. I wish to colour 10 cubic metres of water, and I do not know which compound to use by preference.—K. Niuman, Valparaiso.

WORCESTERSHIRE COUNTY COUNCIL.

ADDITIONAL COUNTY ANALYST.

The SANITARY COMMITTEE of the WORCESTERSHIRE COUNTY COUNCIL are prepared to receive Applications from duly qualified persons for the Appointment of an additional County Analyst for the Administrative County of Worcester (exclusive of the County Boroughs of Worcester and Dudley) under the Sale of Food and Drugs Act, 1875, and the Fertilisers and Feeding Stuffs Act, 1893.

Salary £400 per annum, payable monthly, together with all necessary out-of-pocket expenses. Applications will only be received from persons between 25 and 40 years of age and capable of carrying out Bacteriological researches. A person qualified to lecture on Chemistry as applied to Agriculture will be preferred. The person appointed will, unless specially arranged to the contrary, have to devote his whole time to the service of the Council, and reside in or near Worcester. He must give security in such amount and of such nature as may from time to time be fixed and approved by the Finance Committee. He will be permitted, with the approval of the Sanitary Committee, to take a limited number of pupils, and must, if required, be prepared to lecture on and teach Analytical and Bacteriological work. He will also be required to do such Analytical and Bacteriological investigations as may be directed by the County Council.

The appointment will be held subject to six months notice on either side, which may be given at any time. No Superannuation or Pension will be paid. Office and Laboratory will be provided by the Council, together with all necessary Books, Stationery, Instruments, Chemicals, and other appliances. He will not be allowed to undertake private research work unless with the consent of the County Council.

The appointment will be subject to the approval of the Local Government Board and also of the Board of Agriculture.

Applications, stating the Candidate's age, where educated, present position, and previous experience (especially as to Analytical and Bacteriological work), must be made in the Applicants' own handwriting on paper of foolscap size, accompanied by not more than Six copies of recent testimonials, addressed to the undersigned and marked "County Analyst," so that it shall be received by 3 p.m. on Friday, the 19th day of August, 1898, and no application afterwards received will be entertained.

It is understood that the person appointed will also be appointed by the Corporation of Worcester to act as Analyst for the City of Worcester at an extra salary.

A printed statement of the duties may be obtained from me. Canvassing in any form will absolutely disqualify.

Selected Candidates will be required to attend a Meeting of the Sanitary Committee of the County Council, notice of which will be given.

The person appointed must be prepared to enter upon his duties not later than 1st October, 1898, and undergo a Medical Examination by an approved person.

S. THORNELY,
Clerk of the County Council.

Shire Hall, Worcester,
12th July, 1898.

The Sulphate of Ammonia Committee

OFFER

THE SUM OF 500 GUINEAS

To be given for the best Essay on the following subject:—

"THE UTILITY OF SULPHATE OF AMMONIA IN AGRICULTURE."

The subject to be treated from a practical and scientific point of view.

The Committee has secured the services of Mr. William C. Little, Member of the late Royal Commissions on Agriculture, and Dr. Voelcker, Consulting Chemist to the Royal Agricultural Society of England, to act as Judges of the Essays sent in. In the event of any difference arising, Mr. Samuel Rowlandson, a Member of the Council of the Royal Agricultural Society of England, will act as referee.

The Essays must be in the English language, and written on one side of the paper only; they must further bear a distinguishing motto or nom de plume, but not the names of the authors.

Each author, when sending in his Essay, must at the same time write his name and address on a slip, which he shall enclose in a separate envelope, seal the letter, and write outside it the motto or nom de plume he adopts for his Essay. The Essay and the envelope containing the slip to be sent in, under one cover, to the undersigned.

The envelopes containing the names of the authors will be opened in the presence of the Committee after the Judges have made their award.

All Essays must be in the hands of the undersigned not later than November 15th, 1898. The selected Essay will become the property of the Committee, who reserve to themselves the right to make such use of it as they may think fit.

The Committee also reserves to itself the right to purchase for a sum not exceeding fifty guineas any of the other Essays.

W. G. BLAGDEN (*Chairman*),
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THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2017.

PREPARATION OF CRYSTALLISED CALCIUM.

By HENRI MOISSAN.

ALTHOUGH calcium is very widely spread throughout nature, it has been impossible up to the present to obtain it pure in any notable quantity. The different methods used for its preparation have only enabled us to collect very small specimens, and its principal properties are far from being well known. Since the researches of Matthiessen it has been considered to be a yellow metal; we shall, however, show later on that it has the same colour as silver.

According to different workers who have been occupied with this subject, its density varies from 1·55 to 1·8. We must further remark that in the various papers treating of the subject of calcium, the authors have not given any analysis of the metal obtained. These several points serve to show the present state of the question.

Historical.

Experiments of Sir Humphry Davy.—The memorable experiment of Sir Humphry Davy on the decomposition of the alkaline earths by the electric current established the existence of a simple metallic body in lime. We know that by the decomposition of lime in the presence of mercury, or by the decomposition of a mixture of moist lime and mercuric oxide, he obtained an amalgam of calcium which decomposes water with great rapidity, re-forming slaked lime. The metal prepared by Sir Humphry Davy was white.

Matthiessen's Method.—By applying Bunsen's ideas (*Ann. der Chim. und Pharm.*, lxxxii., p. 137), Matthiessen (*Ibid.*, xciii., p. 277, 1855) succeeded in electrolysing a mixture of equal molecules of chloride of lime and chloride of strontium; under these conditions he obtained small metallic globules of a yellow colour. This experiment can easily be repeated, but it only gives very small returns; we have repeated it under the conditions laid down by Matthiessen, and also by increasing the size of the apparatus and the intensity of the current, but the returns were always of the smallest. The metal obtained certainly possesses a more or less pronounced yellow colour, resembling the colour of bell-metal.

Method of Liès-Bodart and Jobin.—In 1858 MM. Liès-Bodart and Jobin (*Ann. de Chim. et de Phys.*, Series 3, vol. liv., p. 363) described a chemical process for the production of calcium. They caused sodium to react on iodide of calcium in a state of fusion in an iron crucible closed with a screw-down cover. We repeated this experiment, but the results are very variable, as much from the point of view of the return obtained as to the purity of the product.

As a rule, by using 300 grms. of anhydrous iodide we can isolate a few metallic globules which together weigh about 6 to 8 grms. A certain proportion of the calcium is in the state of minute globules, distributed throughout the mass, and so small that they cannot be isolated.

Further, in some experiments, such as described by MM. Liès-Bodart and Jobin, we find globules of sodium not containing any calcium, as well as others of a yellow colour more or less rich in calcium, all mixed up together. If we analyse the metallic portions rich in calcium, we find that they contain very variable quantities of this metal. We obtained the following figures from the richest portions;—Ca per cent, 83·00, 88·30, 88·70, 93·20,

Temperature has a great influence on the returns.* If the reaction takes place at a dull red heat, the quantity of sodium contained in the metallic globules varies from 10 to 20 per cent, and the return is greater. If, on the contrary, the temperature is raised, and reaches a bright red, we obtain a metal containing a higher proportion of calcium, but the return is much lower.

Finally, when the heat is too great in the Liès-Bodart and Jobin method, we get no calcium at all; a new reaction takes place, to which we shall refer later on.

Sonstadt's Process.—Sonstadt (*Proc. Lit. and Phil. Soc. of Manchester*, 1864, p. 243) has applied the Liès-Bodart and Jobin reaction, by making the sodium react on a mixture of chloride of calcium and iodide of potassium. In this experiment we find, on the surface of the ingot of melted salts, a well melted, united metallic mass, which can be detached without any difficulty. This metal is brittle, with a crystalline texture, more often pyrophoric; it contains a notable quantity of the alkaline metals sodium and potassium. We repeated this operation four times, and the proportion of calcium in the metal never exceeded 20 per cent.

Caron's Method.—Caron (*Comptes Rendus*, vol. l., p. 547) has prepared calcium by reducing chloride of calcium by sodium in the presence of metallic zinc. An alloy of zinc and calcium is formed, which, when heated in a carbon crucible, leaves behind calcium which possesses the yellow colour of brass.

Winckler's Process.—M. Winckler (*D. Chem. G.*, vol. xxiii., pp. 44 and 120) first experimented on the reduction of lime by magnesium in a current of hydrogen gas; but he did not separate the calcium obtained from the magnesia. In a second paper (*D. Chem. G.*, xxiv., p. 1966) he deduced the formation, under the preceding conditions, of a hydride with the formula CaH, from the complex composition of the mixture remaining in the crucible; he did not, however, isolate any product.

To sum up, the difficulties met with in these different processes, and which prevent us obtaining calcium in a state of purity, are the following:—

1st. The separation of the calcium cannot be effected by the distillation of its amalgam; the residue is always impure.

2nd. By the electrolysis, by the dry method, of mixtures of salts of calcium and alkaline salts, it is the alkaline metal that is first set at liberty, and which then reacts more or less during electrolysis.

3rd. In the reduction by sodium there is always a mixture of sodium and calcium produced, since this latter metal, because of its reducing properties, acts in its turn on the salts present in the mixture. It forms an equilibrium varying according to the temperature and the bodies present in the reaction.

4th. Finally, whatever the method employed, it is impossible to distil the mercury or the excess of the alkaline metal in a current of hydrogen or of nitrogen.

With hydrogen the calcium produced rapidly forms, as we shall see later on, a perfectly white hydride with the formula CaH_2, and with nitrogen it forms a crystalline nitride. Hydrogen and nitrogen must therefore be absolutely kept away in all experiments on the preparation of calcium.

Preparation of Crystallised Calcium.—This preparation can be carried out by two distinct processes:—

1st. To obtain calcium in a state of purity we utilised the property this metal possesses (unknown up till now) of dissolving in liquid sodium kept at a dull red heat. On cooling, the calcium crystallises in the midst of the sodium, and by treating the metallic mass with absolute alcohol there remain brilliant white crystals of pure calcium of a hexagonal form.†

* We repeated this experiment of MM. Liès-Bodart and Jobin ten times. In one operation we distilled the greater part of the sodium used, and we obtained a metallic ingot weighing 12 grms., containing 88 per cent of calcium.

† The calcium soluble in liquid sodium at a dull red heat is almost insoluble in this metal at its point of solidification.

The following is our method of working:—In an iron crucible of 1 litre capacity we place 600 grms. of crystallised anhydrous iodide of calcium and 240 grms. of sodium. The proportion of the alkaline metal present is three times as much as is required by the reaction—

$$CaI_2 + Na_2 = Ca + 2NaI.$$

The anhydrous crystallised iodide of calcium is roughly powdered, then mixed with pieces of sodium cut to about the size of a nut; the crucible is tightly closed by means of a screw-down cover, then kept for about an hour at a dull red heat. It is as well to agitate the crucible by a slight rotatory movement by means of a pair of tongs.

At the commencement of the operation a small quantity of the vapour of sodium escapes between the crucible and the lid; but, as the upper part gets heated less than the lower, as soon as the first disengagement of heat due to the reaction is finished, a little liquid sodium condenses in the thread of the screw, and the sealing of the joint is complete.

After cooling, the crucible is opened; it contains a layer of melted salt of a blue colour, surmounted by a metallic cake of sodium.

To separate the calcium we place about 500 c.c. of absolutely anhydrous alcohol in a flask of 1 litre capacity, kept cool by melting ice. The sodium taken from the crucible is thrown in in lumps of about 1 c.c. each. When all disengagement of hydrogen has ceased, we decant the liquid portion, and replace it with the same quantity of absolute alcohol.*

This washing is continued until the alcohol no longer leaves any fixed residue on evaporation. The brilliant powder remaining at the bottom of the flask is treated with anhydrous ether (previously kept over sodium), then placed in a glass tube, and dried at the ordinary temperature by a current of perfectly dry carbonic acid or hydrogen gas. The specimen should then be immediately sealed up in a glass tube.

It is necessary in all these operations to take the greatest precautions against the action of moisture and contact with air. This very finely divided crystalline powder oxidises with the greatest facility.

The return is about 50 per cent of the theoretical weight of the calcium used in the experiment. In our first experiments we obtained about 40 grms. of calcium at each operation.

2nd. We can also obtain calcium, either in crystals similar to those just described or in little melted globules, by means of the electrolysis of fused iodide of calcium at a dull red heat. This salt is a very good conductor of electricity. The negative electrode is of pure nickel, and the positive electrode—consisting of a cylinder of graphite—is placed in the axis of a porous pot. The temperature is maintained by the current at about the melting-point of iodide of calcium, which allows of the easy escape of the vapour of iodine. Under these conditions we obtain a white melted or crystalline metal. We are pursuing the study of this electrolysis.

Analysis.—To estimate the calcium in the metal prepared by the first process, we take a known weight and carefully decompose it by water. The hydrate of lime is dissolved in a few drops of nitric acid, the liquid is exactly neutralised with ammonia, and the calcium precipitated in the form of oxalate.

From the weight of quicklime obtained after filtration and calcination, the calcium is calculated. We obtained the following figures:—Calcium per cent, 98·9, 99·1, 99·2. —*Comptes Rendus*, cxxvi., No. 25, June 20, 1898.

Heat of Formation of the Meta- and Para-oxybenzoates of Soda.—G. Massol.—These were determined by observing the heats of solution in water of the anhydrous neutral salts of soda, $C_7H_5O_3Na$; from these the heats of formation of the solid salts of soda, starting from the acid and the solid bases, were calculated.—*Bull. de la Soc. Chim. de Paris*, xix.-xx., No. 6.

* The alcohol has been first rid of air by boiling *in vacuo* at a low temperature, and then saturated with pure dry hydrogen gas.

ON THE PREPARATION AND PROPERTIES OF A NEW CARBIDE OF TUNGSTEN.

By P. WILLIAMS.

We have attempted to prepare double carbides of iron with a certain number of allied metals, such as chromium, molybdenum, tungsten, &c., and in examining the double compounds of tungsten and iron we have succeeded in isolating a new carbide of tungsten.

M. Moissan has described a compound (*Comptes Rendus*, cxxiii., p. 15) answering to the formula W_2C, which he obtained by heating tungsten with an excess of carbon in the electric furnace. This body is attacked by chlorine; but the new body is, on the contrary, clearly distinguished from this one, as chlorine has no action on it whatever. Its formula is WC. The present paper was written for the purpose of making known its preparation and principal properties.

Preparation of Carbide of Tungsten.

Carbide of tungsten, WC, may be obtained by one or other of the following methods:—

1. We make an intimate mixture of pure calcined tungstic acid, iron, and petroleum charcoal, in the following proportions:—

Tungstic acid	120 grms.
Charcoal	20 ,,
Iron	150 ,,

The mixture, placed in a carbon crucible, is heated to a reddish white heat by means of a powerful forge, for an hour. After cooling, we find a well melted button of iron at the bottom of the crucible; it is very hard and of a crystalline appearance. This button contains the carbide of tungsten mixed with a large quantity of iron and the double carbide.

To separate the carbide from the excess of iron, the button is attacked with warm hydrochloric acid until it is completely disintegrated. There remains a mixture of the double carbide of tungsten and iron, and of carbide of tungsten. We can separate the greater part of the simple carbide of the double compounds of iron and tungsten by means of a magnet, carbide of tungsten not being magnetic. This carbide is still mixed with graphite, but the great difference in the densities of the carbide and of graphite enable us to separate them very easily by levigation. The last traces of impurities are removed by a current of chlorine at a red heat. Finally, the use of bromoform or of iodide of methylene enables us to separate the small quantity of graphite which might have been liberated during the treatment with chlorine.

2. We can also prepare the carbide in the electric furnace. The same mixture, heated for five or six minutes with a current of 900 ampères and 45 volts will give a well melted button, easily broken, and also containing a good deal of graphite. The separation of the carbide is effected in the manner already described.

The crystals of the carbide prepared by the electric furnace are larger than those which we obtained by the use of the forge. The return is very small in either case; the carbide is found principally round the periphery of the button. We thought that this might be due to more rapid cooling; we therefore plunged the button, immediately on withdrawing it from the furnace, into a vessel filled with cold water, as described by M. Moissan in his experiments on the production of the diamond and of carbide of iron. In this manner we obtained a much greater yield, but the crystals were less well-defined.

Physical Properties.—Carbide of tungsten occurs in the form of an iron-grey powder; when examined under the microscope it is seen to be formed of non-transparent cubical crystals. It is very hard, and easily scratches quartz. The density at 18° is 15·7.

Carbide of tungsten melts with great difficulty. A small quantity was placed in a crucible of retort carbon

and well closed; it was then heated for a quarter of an hour with a current of 950 ampères and 45 volts. The carbide WC was partially liquefied and transformed into W_2C and graphite, as shown by the analysis of the melted portion.

Chemical Properties.—Carbide of tungsten heated to a red heat in a current of pure dry hydrogen does not undergo any change. Heated in the presence of oxygen or of air it oxidises slowly, with the formation of tungstic and carbonic acids. Nitrogen is without action at a red heat.

Fluorine attacks it in the cold with incandescence, but chlorine, iodine, and bromine are entirely without action on the carbide even at a red heat. The gaseous hydracids and their solutions in water do not attack it. When heated with hydrochloric acid in a sealed tube for three hours, at a temperature of 350° C., there is no action between the carbide and the acid; but a considerable quantity of crystals of chloride of sodium separate out on cooling, on account of the glass having been attacked.

Nitric and sulphuric acids attack the carbide very slowly.

There is no action between water and carbide of tungsten up to the temperature of the softening of Bohemian glass. It is easily oxidised when heated with chlorate or nitrate of potassium; the bisulphate and the carbonate of potassium only attack it very slowly.

Analysis of Carbide of Tungsten.—The carbon is estimated by burning the carbide in a current of oxygen. The carbonic acid formed is absorbed in weighed potash tubes.

The tungsten is estimated by the oxidation of the carbide in a current of air; the tungstic acid thus formed is then weighed.

We have obtained the following figures:—

	I.	II.	III.	Calculated for WC.
Tungsten ..	93·55	93·52	93·60	93·88
Carbon ..	5·87	6·20	6·08	6·12

To sum up, we have prepared a carbide of tungsten of the formula WC. This carbide is formed when we heat a mixture of tungstic acid and carbon with a large excess of iron at the temperature of the electric furnace. In the presence of tungstic acid and carbon only, the carbide W_2C only is formed as described by M. Moissan.

Consequently, in the presence of carbide of iron, it is possible to obtain a compound of tungsten which contains twice as much carbon as that obtained by merely heating tungsten and carbon together. The iron, by facilitating the fusion of the mass, enables us to prepare this compound at a temperature lower than the fusing-point of tungsten, at which temperature the carbide WC only is formed.—*Comptes Rendus*, cxxvi., No. 24, June 13, 1898.

ON THE

ACTION OF SODAMMONIUM IN EXCESS ON RED PHOSPHORUS.

By C. HUGOT.

The results of the action of phosphorus in excess on sodammonium have already been published (*Comptes Rendus*, cxxi., p. 206). The action of sodammonium in excess on phosphorus gives rise to a compound the study of which is the object of this paper.

The apparatus used in these experiments consists of a tube containing recently melted soda, in which pure ammonia gas is liquefied. On contact with the sodic hydrate the liquid ammonia is completely dehydrated. The tube R, which serves as a reservoir for the ammonia gas, is closed by a glass tap. It is connected on the one hand with a mercury manometer, and on the other with the apparatus in which the reaction is to take place. On the small arm a tube is sealed, provided with a tap facilitating the collection over mercury of the gases disengaged during the experiment.

The apparatus in which the reaction of the phosphorus on the ammonium takes place is made entirely of glass. It is practically in the form of an H, of which the vertical sides are formed by the two tubes A and B, and the horizontal part by a narrow T tube plugged with dry glass wool.

The lower ends of the tubes A and B are drawn down fine, and for the weighings may be fitted with corks. The upper ends of A and B are both furnished with glass taps. It is by the tube A that the apparatus communicates with the reservoir of ammonia gas described above.

The following is the plan adopted for carrying out an experiment:—

The apparatus, A, T, B, carefully dried, is put in communication with the reservoir R. A current of ammonia gas traverses the apparatus, and completely drives out the air contained therein. The lower extremities are closed with corks, and the apparatus is weighed, full of ammonia.

We then introduce successively into the tube A a morsel of red phosphorus, well washed, and dried in a current of ammonia gas, and a globule of sodium, weighing the whole apparatus each time, full of ammonia gas as before. The sodium is introduced in the melted state in an atmosphere of pure dry hydrogen, after having been previously purified by distillation.

The weights of the phosphorus and the sodium being thus known, the lower extremities of the tubes A and B are sealed before the blowpipe. Communication is re-established between the reservoir and the apparatus which is plunged into a freezing mixture; sodammonium is formed, and dissolves in the excess of liquefied ammonia gas.

The phosphorus enters into reaction with the sodammonium. The liquid, which is at first of a reddish brown colour, slowly becomes greenish. This greenish tint is more or less bright, according to whether the phosphorus is present in greater or less proportion with regard to the sodium. We notice, at the same time, the formation of small brilliant crystals on the inner surface of the tube A.

During this operation, and especially after several hours' contact, hydrogen is given off, and may be collected over mercury.

After standing for a day, the apparatus being kept in melting ice, we caused the greenish liquid to pass from the tube A, through the glass wool, into the tube B, by inclining the apparatus. A large part of the excess of sodammonium passes over.

We then drive off the liquefied ammonia gas from B into A by distillation, by warming B and cooling A. We then run more liquid from A into B through the glass wool, or, in other words, we wash out the tube A with liquefied ammonia gas.

This operation should generally be repeated at intervals for several days, so as to remove the last traces of sodium, which suffice to colour the liquid a greenish blue. A crystalline powder of a yellow appearance remains in the tube A. If we allow these crystals to soak for some time in liquid ammonia, we notice that it takes a yellow tint. The washing of this crystalline powder can be carried out in the manner described above.

Still keeping the apparatus at 0°, the ammonia is gradually allowed to escape; there then remains a yellow deposit in B, which coats the inner surface of the tube, as well as crystalline sodium produced by the dissociation of the excess of sodammonium.

The yellow body contained in the tube B corresponds to the formula $P_2H_3Na_3$.

The crystals in the tube A, having a pale yellow colour, are crystals of amidide of sodium mixed with traces of the body $P_2H_3Na_3$.

If we analyse these crystals, after having washed them

for several days in liquefied ammonia gas, we find that they correspond to the formula NH_2Na. The reaction which takes place in the tube may be represented by—

(*a*) $6NH_3Na+2P=P_2H_3Na_3+3NH_2Na+3NH_3$.

The quantity of amidide of sodium formed is given by the weight of the crystals remaining in A. It is necessary to subtract the weight of the amidide formed by the spontaneous decomposition of the sodammonium noticed by M. Joannis (*Comptes Rendus*, cxii., p. 392). This quantity can be arrived at by estimating the hydrogen given off during the operation and collected over mercury. The yellow body, treated by acids and water, gives rise to the following reactions:—

(*b*) $P_2H_3Na_3+3HCl=3NaCl+2PH_3$.

(*c*) $P_2H_3Na_3+3H_2O=3NaHO+2PH_3$.

The phosphorus is deduced from the quantity of phosphide of hydrogen given off when we allow pure or slightly acidulated water to act slowly on the preceding body. The excess of sodium is known by the volume of hydrogen given off in these same reactions.

Heated *in vacuo*, the body $P_2H_3Na_3$, after having lost the small amount of ammonia gas it retained, gives off phosphide of hydrogen and a little hydrogen at about 100°. From 150° to 200°, on the contrary, the proportion of phosphide of hydrogen diminishes considerably; and, finally, at 200—300° the gas collected is only hydrogen.*

So as not to prolong these washings in liquid ammonia to too great an extent, it would appear, according to the formula (*a*) more convenient to cause the reaction between the sodium and the phosphorus to take place in proportions hardly higher than 3 to 1. Experience shows, however, that if we do not use a sufficient excess of sodium, the reaction (*a*) is not the only one that is produced. We have noticed the formation of compounds difficult to determine. We can, however, affirm the presence of the body PH_2Na to which M. Joannis (*Comptes Rendus*, cxix., 557) gave the name of phosphidide of sodium. — *Comptes Rendus*, cxxvi., No. 24.

NOTE ON LIQUID PHOSPHORUS.

By F. P. VENABLE and A. W. BELDEN.

IN 1875 Hourton and Thompson (*Arch. de Pharm.*, 3, 6, 49), reported the formation of a peculiar modification of phosphorus formed on boiling ordinary phosphorus for five minutes with a strong solution of potash. The alkaline solution was poured off and the liquid phosphorus washed. It is said to remain liquid for months and solidifies only on cooling to +3·3°. It is further reported as not oxidising in the air nor giving off light in the dark. On becoming solid it forms ordinary wax-like phosphorus and a second variety of crystalline phosphorus.

These singular statements are cited in Dammer's "Handbuch der anorganischen Chemie," and the chemical literature available to us has been searched in vain for any further mention of this strange variety of phosphorus. It has, therefore, seemed advisable to give a brief notice of some experiments in which it was attempted to form this liquid phosphorus.

Five grms. of fresh wax phosphorus were placed in a flask with 80 c.c. of a saturated solution of potassium hydroxide and boiled for five minutes in a neutral atmosphere (nitrogen was used). This was washed with water at 19° and on the second washing the phosphorus solidified. If the alkaline solution was poured off directly, the phosphorus caught fire; hence it was usually poured off to small bulk, diluted with water, and again poured off, and so on, until the phosphorus was washed. In every experiment performed the phosphorus solidified after the second or third washing. The amount of phosphorus, the time of boiling (three, five, ten, and fifteen minutes), and the strength of the potassium hydroxide solution (saturated to 10 per cent solution), were each varied without securing the liquid phosphorus.

It is, however, true that the phosphorus becomes liquid on heating under the alkaline solution, and, if left covered with the same, stays liquid a long time, solidifying only when strongly cooled. It seems to give off occasional bubbles of gas during this standing and is probably being slowly changed into phosphine at ordinary temperatures. We are quite at a loss to know how the authors mentioned above secured their liquid phosphorus and how it could prove unalterable in the air. In all of our experiments it was peculiarly inflammable.—*Journal of the American Chemical Society*, vol. xx., No. 4.

* The sum of the weights of the pure hydrogen and the hydrogen corresponding to the phosphide of hydrogen represents exactly the theoretical quantity of hydrogen contained in $P_2H_3Na_3$.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 11th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us, all were found to be clear, bright, and well filtered.

The rainfall at Oxford for the month of June is again considerably below the average; the actual fall being 1·34 inches; the thirty years' average is 2·11 inches, leaving a deficiency of 0·77 inch. This brings the deficiency for the first six months of this year to 3·34 inches.

Our bacteriological examinations of 252 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, standpipes, &c., making a total of 291 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	390
New River, filtered (mean of 25 samples) ..	54
Thames, unfiltered (mean of 26 samples) ..	2321
Thames water, from the clear water wells of five Thames-derived supplies (mean of 124 samples)	57
Ditto ditto .. .. highest	2108
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	2149
River Lea, from the East London Company's clear water well (mean of 25 samples) . ..	33

During the month the London waters have been of high dietetic quality. The number of microbes in the supply has been generally low, with the exception that on the 6th of June a sudden increase of harmless microbes took place in all the Companies' waters. The fact that this anomaly occurred simultaneously in all the filtered waters, suggests that it was due to some general cause, which at present remains unexplained.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A METHOD FOR ESTIMATING PERCHLORATE IN NITRATES OF SODA AND POTASH.

By N. BLATTNER and J. BRASSEUR.

In their researches, carried out at Messrs. Kuhlmann's laboratory at Loos, on the presence and the influence of perchlorate in nitrates, MM. Blattner and Brasseur were led to search for a method of estimation which would be more simple and more exact than those already known. The following is what they have found:—

The chlorine in the chloride of sodium is first of all estimated in the ordinary way: 5 or 10 grms. of the nitrate under examination are then weighed while dry and finely pulverised; this is mixed with 8 or 15 grms. of pure lime, obtained by the calcination of pure precipitated carbonate of lime. The mixture is placed in a platinum or porcelain crucible, which must be covered and heated for fifteen minutes with a Bunsen burner. After cooling, the contents of the crucible are turned out into a flat-bottomed flask, and dissolved in dilute nitric acid free from chlorine.

In the solution the chlorine is estimated by nitrate of silver, either in acid solution according to Volhard's method, or in a solution neutralised by carbonate of lime, or by weighing the chloride of silver.

We thus obtain the chlorine in the chloride, the chlorate (if any is present), and in the perchlorate.

By difference with the first result, the proportion of perchlorate is calculated.

This method, which is simple and rapid, is at the same time perfectly exact. The following are a few results obtained with artificial mixtures of pure nitrates of soda and potash, with known varying proportions of perchlorate of potash:—

	Found.
Mixture with 1 per cent of perchlorate	1·010 per cent
,, 2 ,, ,,	2·026—2·012 ,,
,, 3 ,, ,,	3·015—3·006 ,,

—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 12.

SOLUTIONS OF SILICATES OF THE ALKALIES.*

By LOUIS KAHLENBERG and AZARIAH T. LINCOLN.

(Concluded from p. 33).

The lithium silicates investigated yielded the figures in Tables VI. and VII. The normal salt is decomposed to the extent of 95·5 per cent at $v=32$, while at $v=48$ the decomposition is practically complete, as in the case of the analogous sodium and potassium salts. The salt $Li_2Si_5O_{11}$ is hydrolytically dissociated 67·7 per cent, and this decomposition is practically complete at $v=128$. The behaviour of the lithium salts, then, is perfectly analogous to that of the potassium and sodium salts.

The determinations made with rubidium and cæsium silicates are given in Tables VIII. and IX. The quantities of these alkalies that were available were small, and hence but few determinations were made. A glance at the results shows that these silicates behave like those of the other alkalies. The solutions investigated were quite dilute, and in them, as the results show, the hydrolytic decomposition had gone on very far. The lowerings obtained with the rubidium salt are greater than they ought to be theoretically. This is probably due to the fact that the rubidium salt, from which the hydroxide of rubidium that was used was prepared, contained some sodium. As the quantity of rubidium salt available was small a special analysis to ascertain the amount of sodium present was not made.

The results of the determinations of the electrical conductivity of the solutions are contained in Tables X. and XI. The former table contains the conductivity of solutions of the free alkalies at 25° C. It was necessary to make these determinations, for the conductivity of solutions of the alkaline hydroxides at 25° C. could not be found in the literature, and only by comparing the conductivity of solutions of the alkaline silicates with that of solutions of the free alkalies, can an idea of the extent of the retarding influence that the colloidal silicic acid has on the movements of the ions, be gained.

Kohlrausch (*loc. cit.*) noticed that on diluting silicate solutions the conductivity changed for a time and finally became constant. The time of this variation and the degree of the latter depended of course on the conditions

Table VII.

$Li_2Si_5O_{11}$. Molecular weight = 329·52.

v.	Freezing-point.	Mol. wt.	Mol. wt. (LiOH).
32	0·172	113·2	16·4
48	0·139	93·3	13·5
64	0·112	86·9	12·6
96	0·077	84·3	12·2
128	0·062	78·5	11·4

$\frac{1}{4}$ of 329·52 = 82·38.

Table VIII.

Rb_2SiO_3. Molecular Weight = 245·38.

v.	Freezing-point.	Mol. wt.	Mol. wt. (RbOH).
64	0·139	52·1	43·2
96	0·098	49·3	40·9

$\frac{1}{4}$ of 245·38 = 61·34. $\frac{1}{2}$ Mol. wt. RbOH = 50·83.

Table IX.

Cs_2SiO_3. Molecular Weight = 339·60.

v.	Freezing-point.	Mol. wt.	Mol. wt. (CsOH).
64	0·102	98·3	86·1
96	0·068	98·3	86·0

$\frac{1}{4}$ of 339·60 = 84·9. $\frac{1}{2}$ Mol. wt. CsOH = 74·38.

Table X.

v	NaOH. λ	KOH. λ	LiOH. λ
1	157·5	—	—
2	181·2	196·7	157·6
4	188·1	207·2	171·0
8	194·7	213·1	179·2
16	197·4	216·7	185·9
32	199·0	219·1	189·3
64	199·1	220·4	189·2
128	199·0	218·4	189·2
256	196·3	215·0	184·0
512	188·9	208·0	174·9
1024	181·8	201·4	170·0

The water used had a specific conductivity of $1·7 \times 10^{-6}$. This has not been deducted in the above table.

* *Journal of Physical Chemistry*, vol. ii., No. 2, February, p. 77 (1898).

Table XI.

v	Na_2SiO_3. λ	$NaHSiO_3$. λ	$Na_2Si_2O_{11}$. λ	K_2SiO_3. λ	$KHSiO_3$. λ	Li_2SiO_3. λ	$Li_2Si_2O_{11}$. λ
8	105·3	72·4	—	—	87·3	—	—
16	112·0	78·8	—	130·9	110·3	—	—
32	117·8	84·9	73·0	176·4	117·6	125·0	55·4
64	115·0	90·1	79·9	182·6	126·2	126·0	61·6
128	119·5	103·7	87·3	185·5	133·4	129·2	67·5
256	95·7	114·2	93·1	187·1	141·7	130·2	72·6
512	91·8	133·1	101·1	191·8	155·9	138·5	78·9
1024	104·8	148·5	113·3	182·5	175·6	145·2	90·6

The conductivity of the water, which was 1×10^{-6}, has been deducted in each case.

of experiment. Kohlrausch investigated this time factor as well as the variation of the conductivity of sodium silicate solutions with the temperature. He found that in some cases equilibrium was established in the solution in a few minutes, in others it took five hours or more. The time effects studied by Kohlrausch were also observed by us, and on the whole we are able to confirm his experiments as far as we went. It was not the purpose of this investigation, however, to study this time effect further, and for this reason the conductivity of the solutions was determined only after equilibrium had become established in them. The strongest silicate solution was prepared as already described, then the various dilutions (v = 16 to 1024) were prepared in thoroughly cleaned and steamed flasks, which were kept tightly corked. The dilutions were made by means of carefully calibrated pipettes. At the end of five to six hours (when equilibrium had practically become established) the contents of the various flasks were quickly transferred to the resistance cell and the conductivity determined.

In Tables X. and XI. v denotes the volume in litres in which one grm.-equivalent of the compound indicated by the formula is contained, and λ denotes the equivalent conductivity expressed as usual in mercury units.

It will be observed that in Table X. the values for λ increase as v increases until they reach a maximum, after which they decrease. This behaviour of the alkaline hydroxide is well known and is to be ascribed to impurities in the water. Table XI. shows that in case of the normal silicates of sodium and potassium the values for λ also pass through a maximum. In case of the acid silicates of sodium and potassium and those of lithium the values for λ do not pass through a maximum. It will be noted that the conductivity of the normal salts is uniformly greater than that of the acid salts of the same metal. The values of λ for v = 256 to 1024 in the case of Na_2SiO_3 are less than those for the acid silicates at the same concentrations; this, however, is undoubtedly due to experimental error. A re-determination of λ for these concentrations was contemplated, but was not carried out, as it is especially difficult to get a mixture of the silicic acid solution and caustic soda in the proportions required by the formula Na_2SiO_3, owing to the fact that the mixture gelatinises just before the entire quantity of alkali has been added.

By comparing the values for λ in Table X. with those of the salt of the corresponding metal in Table XI. the effect of the presence of the silicic acid on the conductivity may be seen. It will be observed that even in the most dilute solutions of the normal salts the values for λ still fall considerably short of equalling those of the hydroxides. The values of λ in Table X. pass through their maximum at about v = 32 to 64; at this concentration then the hydroxides are practically completely dissociated. It will be recalled that from the cryoscopic determinations on the normal silicate solutions it was inferred that in the latter hydrolytic decomposition is practically complete at v = 48. Although the errors of measurement in the freezing-point determinations are greater than in the measurement of the electrical conductivity, yet it would appear safe to say that the increase in the value of λ for the silicate solutions beyond v = 64, is mainly due to a decrease of the retarding influence of the silicic acid on the movements of the ions.

The conductivity of solutions of cæsium and rubidium silicates was also determined. Unfortunately the water used in making the dilutions had become contaminated, a fact which was later discovered, and hence the figures obtained are not given here. It may be stated, however, that the figures obtained showed beyond any reasonable doubt that the silicates of these alkalies behave in a manner entirely analogous to that of the silicates of the other alkalies.

Summary of Results and General Remarks.

The results of the foregoing investigation may be briefly summarised as follows:—

1. The conclusion of F. Kohlrausch that in solutions of sodium silicates these salts are hydrolytically decomposed into sodium hydroxide and colloidal silicic acid, has been confirmed by investigating the freezing-points of such solutions.

2. The freezing-points and the electrical conductivity of solutions of the silicates of potassium, lithium, rubidium, and cæsium show that these salts are also decomposed by water into the colloidal silicic acid and the hydroxide of the alkali metal. The silicates of the alkalies all show an analogous behaviour when dissolved in water.

3. The same solution results whether a silicate is dissolved in water or whether solutions of caustic alkali and colloidal silicic acid in proper proportions are mixed.

4. Since colloidal silicic acid has but little effect on the freezing-point the degree of hydrolytic decomposition of the silicates can be calculated from the lowering of the freezing-point of their solutions.

5. Silicates of the general formulæ M_2SiO_3 and $MHSiO_3$ are practically completely hydrolytically dissociated when one grm.-molecule is contained in 48 litres. Silicates of the general formula $M_2Si_2O_{11}$ are practically completely decomposed by water when one grm.-molecule is present in 128 litres.

6. A comparison of the electrical conductivity of silicate solutions with that of the solutions of the alkaline hydroxides, shows that the values of the former approach the latter as the solutions become more dilute, the retarding influence that the silicic acid has on the mobility of the ions gradually becoming less.

The conclusions here arrived at are of general interest inasmuch as silicates occur in greater or less quantities in almost all natural waters. If the silicates of the alkalies are so easily decomposed by water, how much more readily would silicates of the alkaline earths and the heavier metals be hydrolytically decomposed, especially since solutions of these salts are always exceedingly dilute because the compounds are so difficultly soluble.

Of the waters of 859 springs in various parts of the United States (see *Bull. U. S. Geol. Survey*, 32, 35, 1886), the one that contains the most silica is that of the Deep Rock Mineral Spring at Oswego, N.Y. According to an analysis made in 1871 by S. H. Douglas it contains the

molecular weight of SiO_2 in grms. in 48·84 litres.* Next to this is Opal Spring in Yellowstone National Park in the Gibson Geyser Basin, for according to an analysis made by Henry Leffmann in 1882, its water contains one grm.-molecule SiO_2 in 65·15 litres. The analyses of the other 857 springs show that the waters of but three of them contain over one grm.-molecule SiO_2 in 140 litres and only fourteen others contain more than a grm.-molecule in 350 litres. The waters of the remaining 840 springs contain much smaller amounts of silica, usually less than one grm.-molecule in 3500 litres.

Justus Roth's (*Allgemeine u. Chemische Geologie*, vol. i.) compilation of the analyses of river waters from different parts of the globe (chiefly European, however) shows that the largest amount of silica was found in the water of the Rhine. A sample taken near Strassburg contained one grm.-molecule SiO_2 in 1250 litres. According to the same authority the Atlantic Ocean contains one grm.-molecule SiO_2 in 531 litres. Of the many analyses of the waters of springs of various kinds located in different parts of the globe that have been collected by Roth, none show a greater content of silica than one grm.-molecule in 80 litres, and of course most of them very much less.

In the face of these facts and the results of the above investigations it appears safe to say that in natural waters silicic acid always occurs in the colloidal state; only in very rare instances are the solutions of the silicates so concentrated that they are not practically completely hydrolytically decomposed. This conclusion will no doubt be of value to the mineralogist and geologist in explaining the formation of various siliceous deposits and the alterations produced in rocks by the action of water. It might also prove to be of value to the plant physiologist in explaining how plants take up various constituents from the soil.

* It seems almost that the figures in the report must be a misprint.

TERRESTRIAL CORONIUM.

Professor Nasini, of Padua, who has been working in conjunction with Signori Anderlini and Salvadori, communicates the following note to the French Academy:—

We have for a considerable time been occupied with an extensive study of the gases emanating from the earth in various parts of Italy with the object of detecting the presence of argon and helium, and possibly of other elements they may contain.

The first part of this work has already been published ("Gas delle terme di Abano," *Gazzetta Chemica Italiana*). We are now completing the study of the gases of the Solfatara di Pozzuoli, Grotta del Cane, Grotta ammoniacale, and of Vesuvius. In the spectrum of those of Solfatara di Pozzuoli, which contain argon, we have found a sufficiently bright line with the wave-length 531·5, corresponding to that of corona 1474 K, attributed to coronium, an element not yet discovered, and which should be lighter than hydrogen. This line has never before been observed in earthly products. Besides, we have noted the following lines:—653·5, 595·5, 536·2.

In the spectrum of the gases gathered from the fumarole of Vesuvius, we have observed the lines 769·5, 631·8, 572·5, 536·5, 441·5, and again 595·5. These lines do not all belong to the spectrum of argon or helium; they show a coincidence or proximity only with some unimportant lines of various elements, such as iron, potassium, and titanium. Considering the conditions of our experiments the presence of these elements in the gases we have studied is not probable. The line 572·5 is near to one of nitrogen, but, being the only visible line of the spectrum of this gas, it cannot be attributed to it. Besides coronium we have thus probably other new elements in these gases.

We are diligently pursuing their investigation.

This is an announcement of the highest interest from a scientific point of view, as at once confirming the results of spectroscopic examination of the sun and adding another proof of the substantial identity of materials in the sun and the earth. Hitherto nothing has been known of the substance which produces the coronal line 1474 K. It has not been observed anywhere in nature except in the corona, its supposed identity with the auroral line having long ago been disproved, although it may possibly be asserted here and there in a text-book not written up to date. Coronium would seem, however, to be a substance with a vapour density far smaller than that of hydrogen, which is by far the lightest body with which we are familiar. Some have suggested that it is only one of the elements known to us, modified in some unknown way by conditions differing enormously from those that obtain on this planet. But against this hypothesis has to be set not only its occurrence at a distance from the sun's body estimated at 300,000 miles, where it is difficult to believe that the vapours of the suggested elements can predominate, but also the fact that in the midst of solar disturbances in prominences or near sun spots, when the lines of hydrogen and other known elements are contorted, this coronal line remains sharp, fine, and straight. From these and other considerations it has been held that the green coronal line is due to a permanent component of the solar atmosphere totally distinct from any element known to terrestrial chemistry. That unknown substance appears now to have been found just where, if anywhere on earth, it might be expected—*i.e.*, in the gases from volcanoes or the springs and minerals subject to volcanic action. It will be observed that even with this addition to the list of known elements the lines in the spectra of the volcanic gases cannot be completely accounted for. It is therefore probable that coronium will be found to be associated with other gases as yet unnoticed.—*The Times*, July 20, 1898.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

Part I.—*Introduction.*

The composition of the ultimate ingredients of the earth's crust—the different mineral species which are there found and of many of which its rocks are made up—was the favourite theme of the great workers in chemistry of the earlier half of this century, and for the painstaking care and accuracy of Berzelius, Wöhler, and others, the mineralogists and geologists of to-day have need to be thankful. Considering the limited facilities at their disposal in the way of laboratory equipment and quality of reagents, the general excellence of their work is little short of marvellous. As an outgrowth of and closely associated with the analysis of minerals, came that of the more or less complex mixtures of them,—the rocks,—to aid whose study by the petrographer and geologist a host of chemists have for many decades annually turned out hundreds of analyses of all grades of quality and completeness. With the growth and extraordinary development of the so-called organic chemistry, inorganic chemistry gradually fell into a sort of disfavour. In many, even of the best, European laboratories the course in mineral analysis, while maintained as a part of the curriculum of study, became but a subordinate prelude to the ever-expanding study of the carbon compounds,

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

whose rapid multiplication, offering an easy and convenient field for original research and possible profit, proved a more tempting opening to young chemists than the often-worked-over and apparently exhausted inorganic pasture. For one student devoting his time to higher research on inorganic lines were perhaps fifty engaged in erecting the present enormous structure of carbon chemistry. The instruction afforded the student in mineral analysis was confined to the ordinary separations of the commoner ingredients occurring in appreciable quantities, with little regard to supposed traces, and with still less attempt to find out if the tabulated list really comprised all that the mineral or rock contained.

With the introduction of improved methods of examination by the petrographer, especially as applied to thin rock sections and the use of heavy solutions, whereby, on the one hand, the qualitative mineral composition of a rock could be preliminarily ascertained with considerable certainty, and on the other, chemical examination of the more or less perfectly separated ingredients was rendered possible, a great help and incentive was afforded to the few chemists engaged in rock analysis. The microscope often obviated in part the necessity for tedious and time-wasting qualitative tests, and the heavy solutions, by permitting the concentration and separation of certain components, facilitated the detection of elements whose existence had long been overlooked.

Meanwhile in the progress of chemistry new methods and reagents for qualitative detection and quantitative separation and estimation were gradually being discovered and devised. The supposed adequacy of some well-established methods was shown to be unwarranted; some had to be discarded altogether; others were still utilisable after modification. In the light thus shed it became possible to explain many hitherto incomprehensible variations in the composition of some rock species or types, as shown in earlier analyses, and in not a few cases it appeared that the failure to report the presence of one or more elements had obscured relations and differences which more thorough examination showed to exist (see pp. 44-45). Consequently there arose a feeling of distrust of much of the older work in the minds of those chemists and petrographers best qualified to judge of its probable qualities. This, and the incompleteness of nearly all the earlier work (and much of that of to-day unfortunately), as shown by the largely increased list of those elements now known to enter into the normal composition of rocks, is rendering the old material less and less available to meet the increasing demands of the petrographer.

And yet these demands on his part are, with few exceptions, by no means so exacting as they should be. Often the analysis is intrusted to the hands of a student without other experience than that gained by the analysis of two or three artificial salts and as many comparatively simple natural minerals, and with a laboratory instructor as adviser whose experience in rock analysis may be little superior to his own. In other words, one of the most difficult tasks in practical analysis is expected to be solved by a tyro, and his results are complacently accepted and published broadcast without question. Even to those thoroughly familiar with the subject, rock analysis is a complex and often trying problem. Although long practice may have enabled one to do certain parts of it almost mechanically, he is still from time to time confronted with perplexing questions which require trained judgment to properly meet and answer, and there is still room for important work in some of the supposedly simplest quantitative determinations. If the results are to be of any decided value for purposes of scientific interpretation and comparison, they should be the product of one competent to find his way through the intricacies of an analysis in which from fifteen to twenty-five different components are to be separated and estimated with close approach to accuracy, and this a beginner cannot hope to do in the majority of cases. The conscientious chemist should have a live interest in this matter. He should work with a twofold purpose in view—that of lightening the labours of those who come after him, by enabling them to use his work with less supplementary examination, and of thereby enhancing his own reputation by meriting encomiums on work that has stood the test of time.

The petrographer, again, should seek to have his analyses made as complete as possible, and not, as is so often the case, be content with determinations of silica, alumina, the oxides of iron, lime, magnesia, the alkalies, and water. The latter, it is true, are entirely justifiable at times, and may serve the immediate purpose for which they were intended; but their incompleteness may, on the other hand, not only conceal points fruitful of suggestion to the attentive mind, but—what is of still greater importance—they may be actually misleading. Enough instances of totally inaccurate conclusions to be drawn from them have fallen under my own observation to fully justify this plea in favour of greater completeness in rock and mineral analyses made for purely scientific purposes.

This is shown by the difference between the following analyses:—

	Earlier analysis.	Later analysis. (*a*)
SiO_2	54·42	53·70
TiO_2	—	1·92
Al_2O_3	13·37	11·16
Cr_2O_3	—	0·04
Fe_2O_3	(*b*) 0·61	3·10
FeO	(*b*) 3·52	1·21
MnO	—	0·04
CaO	4·38	3·46
SrO	—	0·19
BaO	—	0·62
MgO	6·37	6·44
K_2O	10·73	11·16
Na_2O	1·60	1·67
Li_2O	Trace	Trace
H_2O below 110° C.	—	0·80
H_2O above 110° C.	(*c*) 2·76	2·61
CO_2	1·82	—
P_2O_5	—	1·75
SO_3	—	0·06
F	—	0·44
Cl	—	0·03
	99·58	100·40
Less O for F		0·19
		100·21

(*a*) A still more recent analysis of another of the series of rocks of which this is an example has shown that this "later analysis" is itself probably incomplete and incorrect in part—incomplete because of the probable presence of 0·2 per cent or more of ZrO_2, incorrect because of the error in Al_2O_3 resulting from having counted the ZrO_2 as Al_2O_3, and from the fact that titanium is not fully precipitable in presence of zirconium by Gooch's method (the one employed). This latter error involves both the TiO_2 and the Al_2O_3.

(*b*) From the fact that repeated determinations of the iron oxides in this and related rocks from the same region show always a great preponderance of ferric oxide, it is not improbable that the figures given for the two oxides in the first analysis were accidentally transposed.

(*c*) In the published analysis it does not appear whether this is total water or—as seems probable—only that remaining above 100° C.

The specimens were taken and analysed at widely separated times and by different persons, it is true, but they were unquestionably from the same rock mass, in which, however much the relative proportions of the different mineral constituents might vary within certain limits, there can be no reason to doubt the general distribution of all the elements shown by the second analysis.

Another instance of similar kind is given below. Here,

again, certain differences are explainable by natural variations in the proportions of the constituent minerals; but it can hardly be doubted that TiO_2, BaO, SrO, P_2O_5, and SO_3 were present in both specimens in approximately the same amounts. In the earlier analysis in this case determinations of some supposed unimportant constituents were purposely omitted or only made qualitatively, with results that cannot be otherwise than fatal to a full comprehension of the mineralogical nature of the rock:—

	Earlier analysis.	Later analysis.
SiO_2	44·31	44·65
TiO_2	Not est.	0·95
Al_2O_3	17·20	13·87
Fe_2O_3	4·64	6·06
FeO	3·73	2·94
MnO	0·10	0·17
CaO	10·40	9·57
SrO	—	(*a*) 0·37
BaO	—	0·76
MgO	6·57	5·15
K_2O	3·64	4·49
Na_2O	4·45	5·67
Li_2O	—	Trace
H_2O below 110° C.	0·77	0·95
H_2O above 110° C.	—	2·10
H_2O by ignition ..	3·30	—
CO_2	—	0·11
P_2O_5	—	1·50
Cl	—	Trace
SO_3	—	0·61
	99·11	99·92

(*a*) Not entirely free from CaO.

In order to more strongly emphasise the importance of completeness in analysis, one fact brought out by the hundreds of rock analyses made in this laboratory may be cited. It has been demonstrated most conclusively that barium and strontium are almost never-failing constituents of the igneous rocks and many of their derivatives of the United States. These amounts are usually below 0·1 per cent for each of the oxides of these metals, but higher amounts are by no means uncommon. Furthermore, the weight of barium is almost without exception in excess of that of strontium. But a still more important point is that the igneous rocks of the Rocky Mountain region, so far as examined, show far higher average percentages of both metals than the rocks from the eastern and the more western portions of the United States. The following examples serve to illustrate certain types of Rocky Mountain igneous rocks:—Of seven rocks forming a Colorado series, six held from 0·13 to 0·18 per cent of BaO, while in the seventh the percentage was 0·43. The SrO ranged from 0·07 to 0·13 per cent for six, and was 0·28 for that one highest in BaO. Of thirteen geologically related rocks from Montana, embracing basic as well as acid and intermediate types, the range of BaO was from 0·19 to 0·37 per cent, with an average of 0·30 per cent. Three others of the same series contained 0·10 per cent or less, while the seventeenth carried 0·76 per cent BaO. The SrO ranged from 0·37 per cent in the last instance to an average of 0·06 for the other sixteen. Certain peculiar rocks from Wyoming carry from 0·62 to 1·25 per cent BaO, and from 0·02 to 0·33 per cent SrO. Surely this concentration of certain chemical elements in certain geographic zones has a significance which future geologists will be able to interpret if those of to-day are not.

While strongly upholding the necessity for more thorough work, necessarily somewhat at the expense of quantity, it is far from the writer's intention to demand that an amount of time altogether disproportionate to the immediate objects to be sought should be expended on every analysis. But it is maintained that in general the constituents which are likely to be present in sufficient amount to admit of determination in the weight of sample usually taken for analysis—say 1 grm. for SiO_2, Al_2O_3, &c., to 2 grms. for certain other constituents—should be sought for, qualitatively at least, in the ordinary course of quantitative work, and their presence or absence noted among the results. If present in little more than traces, that knowledge alone may suffice, for it is often more important to know whether or not an element is present than to be able to say that it is there in amount of exactly 0·02 or 0·06 per cent. In the tabulation of analyses a special note should be made in case of intentional or accidental neglect to look for substances which it is known are likely to be present. Failure to do this may subject the analyst to unfavourable criticism, when at some future time his work is reviewed and the omissions are discovered by new analyses.

Finally, whenever possible, a thorough microscopical examination of the rock in thin section should precede the chemical analysis. This may be of the greatest aid to the chemist in indicating the presence of unusual constituents, or of more than customary amounts of certain constituents, whereby, possibly, necessary modifications in the analytical procedure may be employed without waste of time or labour.

(To be continued).

NOTICES OF BOOKS.

A Course of Practical Chemistry, or Qualitative Chemical Analysis. By the late W. G. Valentin, F.C.S. Edited and Revised by W. R. Hodgkinson, Ph.D., F.C.S., &c., Professor of Chemistry and Physics in the Royal Military Academy and Artillery College, Woolwich. Ninth Edition. Pp. 403. London: J. and A. Churchill. 1898.

We are glad to welcome yet another edition of this excellent and well-known work. It is many years since the first edition appeared, and, as time has gone on, so has this book gone on "with the times," dropping parts which were of little value, and, so to say, filtering itself, while at the same time keeping up with all that is new in this particular branch of chemical science.

The plan of the book is the same as in previous editions, and is familiar to all chemists; the principal alteration in this edition being the addition of an extra chapter, or rather appendix, in which simple quantitative, including volumetric, operations are dealt with.

More experimental matter has been added, and this is a point to be remembered and dwelt upon, as there is no doubt that a young student will retain far more knowledge if he has to do practical work with his own hands than by merely reading for so many hours a day, getting ready for the inevitable "exam."

Dr. Hodgkinson is not wedded to the "cram and exam." idea, but, on the contrary, takes a keen personal interest in each and all of his pupils, and should be able to "place" them in as satisfactory an order as any examiner.

We cordially recommend this book to beginners in chemistry, as well as to those who have reached a more advanced stage, while at the same it will always be useful as a book of reference.

Elementary Chemistry, Practical and Theoretical. First Year's Course. By T. A. Cheetham, F.C.S. London: Blackie and Sons, Lim. 1898. Pp. 128.

This book, like so many others, is purely for the beginner in chemistry. It commences with exercises in manipulation, the first 65 pages being devoted entirely to labor-

atory—that is, experimental—work, after which we come to the more theoretical side of the subject.

In the two chapters on air, its synthesis, &c., we are rather surprised to find no mention of any gas beyond oxygen and nitrogen; surely it is long enough ago since argon was discovered for inclusion in a new text-book, even if the more recently announced elements are rather shadowy. This is, however, not a matter of great importance. Taking it altogether the book is conveniently planned, and is written in a clear and intelligible manner, and should fulfil the purpose for which it was written.

The Theory and Practice of Electrolytic Methods of Analysis. By Dr. Bernhard Neumann. Translated by J. B. C. Kershaw, F.I.C. London and New York: Whittaker and Co. 1898. Pp. 254.

In the translator's preface we read that only a small number of corrections and alterations from the original have been found necessary, and these were made with the author's consent; the portion of the original work dealing with primary and secondry batteries, the dynamo, and the thermopile, has been omitted, and the electro-chemical equivalents have have been re-calculated upon the most trustworthy figures for the atomic weights of the elements.

The book is divided into three parts. Part I. is on the theory of electrolysis, and deals with Faraday's law, the constitution and conductivity of the electrolyte, the chemical and molecular changes during electrolysis, &c.

Part II., which is subdivided into sub-sections A and B, is on the measurement and regulation of the current. In Section A we find illustrated descriptions of all the well-known instruments used for current measurement, with instructions how to use them; Section B, which is of considerably more importance, is on regulating the current.

We then come to Part III., on the Electrolytic Procedure, divided into four sections:—A. Introductory; B. The deposition of metals from solutions of pure salts; C. Separation of the metals; and D. Practical examples. These four sections really comprise the pith of the book. The metals are dealt with *seriatim*, and all details and data for securing the best results are adequately given. Beginners should be reminded that a certain amount of discrimination is required as to when the electrolytic method may be employed with advantage over the chemical gravimetric method. In many cases the chemical method is preferable, especially if the greatest care has not been taken on the preparation of the electrodes. The current strength (E.M.F.) is another point which requires minute attention, as a very little increase beyond the proper strength will often entirely alter the character of the results.

On page 246 a useful table will be found, giving the theoretical percentage of the metals present in a certain number of metallic salts. The book closes with two indices—one for names, and the other for subject-matter.

CORRESPONDENCE.

THE NEW GASES.

To the Editor of the Chemical News.

Sir,—I observe that Professor Ramsay and his friends, at the fag-end of a letter to *Nature*, reply in an airy manner to the observations made by "Puzzled" in the Chemical News. They account for the attribution to metargon in Paris of a line ascribed to neon in London, by saying that there is a misprint in the *Comptes Rendus*. I have taken the trouble to look up the reference and I find that no possible correction of a misprint of names will meet the case. The line 5849·6 is given as characteristic of metargon in the midst of a description applying solely to that gas. To put neon for metargon in the only possible place, would transfer the whole paragraph to neon, and so make confusion worse confounded. On the other hand, if the misprint is supposed to occur in the figures designating the line in the spectrum, it is rather odd that Professor Ramsay does not mention the correct wave-length.

It would, perhaps, have been better had Professor Ramsay taken the letter of "Puzzled" with sufficient seriousness to reply deliberately in the journal where it appeared. This off-hand reference to a misprint for which there is no room, coming at the end of a rather inconclusive disquisition upon the unfortunate resemblance of the metargon spectrum to that of carbon, does not tend to strengthen public confidence in his general accuracy.—I am, &c.,

Suum Cuique.

THE YEARLY INDEX TO "THE JOURNAL OF THE CHEMICAL SOCIETY."

To the Editor of the Chemical News.

Sir,—I think that many others besides myself must suffer great inconvenience owing to the delay in the publication of the yearly index to the *Journal of the Chemical Society*. Although nearly seven months have elapsed since the completion of the last volume, the index is still not ready for publication. Not only does this prevent the binding of the volume, but renders the journal for 1897 practically valueless for reference. As I have addressed numerous unavailing remonstrances to the Secretary of the Chemical Society, I trust you will be kind enough to publish this note in the hope that some more general expression of opinion may be elicited.—I am, &c.,

A Fellow of the Chemical Society.

July 16th, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 5.

Action of Alkaline Sulphites on the Chromic Salts.—A. Recoura.—If we add to a solution of a chromic salt a large excess of sulphite of sodium, we obtain a liquid in which the chromium has lost the greater part of its usual reactions. In such a solution, soda, carbonate of soda, ammonia, and sulphide of ammonium do not produce the precipitate of chromic hydrate which would come down in an ordinary solution of the salts of chromium. The author concludes that the cause of this anomaly is the immediate formation of a basic sulphate of chromium (these experiments were made with the sulphate) which unites with a certain number of molecules of sulphite of sodium, a number which cannot be exactly determined as the substance will not crystallise.

On Chloral-ammonia.—Marcel Delépine.—As chloral-ammonia cannot be volatilised without decomposition, the author had recourse to cryoscopy to decide what its true molecular weight is: he used successively benzene, acetic acid, and bromide of ethylene; but unfortunately the variations in passing from one solution to another are such that no very good results were recorded. However, two figures were obtained: M = 329 for a concentration of 3 per cent with benzene, and M = 335 with bromide

of ethylene. To reconcile these results with Schiff's formula, both the benzene and the bromide of ethylene must be considered as allowing aggregates of molecules to be substituted, while they do not exist in acetic acid.

Thermo-chemistry: Hydramides and Isomerous Bases.—Marcel Delépine.—Recently distilled anisic aldehyd, $C_8H_8O_2$, boiling at 248—249°, gave as heat of combustion per grm., 7096·0, 7117·2, and 7110·1, average 7107·8 cals. That is, one molecule = 136 grms. The heat of combustion is:—

At constant volume	966·7 cals.
,, ,, pressure	967·3 ,,

Heat of formation—$C_8 + H_8 + O_2 = C_8H_8O_2$ (liquid) .. .. +63·1 ,,

The following heats of formation have also been found:—Anishydramide $(C_8H_8O)_3$, N_2(cryst.) = 48·4 cals.; anisine, $C_{24}H_{24}N_2O_3$ (solid), = +64·6 cals.; furfuramide $(C_5H_4O)_3N_2$ (cryst.), = +0·35 cals.; furfurine, $C_3H_{12}N_2O_3$ = 17·9. There is always a disengagement of 2×11 cals. for the formation of hydrobenzamide, and 13·9 cals. for its transformation into amarine.

Action of Bromine on Tetrabromide of Acetylene in the presence of Bromide of Aluminium. Preparation of Hexabromethane (C_2Br_6).—A. Mouneyrat.—The preparation of hexabromethane by the action of bromine and bromide of aluminium on tetrabromethane is described; it is rather a long process, but gives good results. The molecular weight of hexabromethane was determined by cryoscopy, using benzene—it was found to be 480; the calculated figure for C_2Br_6 is 504.

The Action of Chlorine on Chloroform in the presence of Chloride of Aluminium, and of Bromine on Bromoform in the presence of Bromide of Aluminium.—A. Mouneyrat.—The chloridising action of chloride of aluminium, and the bromidising action of bromide of aluminium in the ethane and in the higher series, shows that these two bodies have the property of creating ethylenic chains. In the methane series such a chain cannot be formed, with the result, from the chloridising and bromidising point of view, that the action is *nil*.

Action of Bromine on Pentachlorethane in the presence of Chloride of Aluminium. Preparation of Dibromotetrachlorethane, $C_2Br_2Cl_4$.—A. Mouneyrat.—This body, prepared from pentachlorethane, is obtained in perfectly defined orthorhombic prisms, smelling slightly of camphor; if left in a dry place they lose their transparency on account of their strong tendency to sublime. Heated in a capillary tube they begin to lose bromine at about 220—225°.

Action of Chloride of Aluminium on Pentachlorethane. Preparation of Bi-chloride of Carbon, $CCl_2=CCl_2$.—A. Mouneyrat.—Bichloride of carbon is obtained simply by heating chloride of aluminium with pentachlorethane; the reaction takes place at 70°, but if the temperature is raised to 100° it goes much more quickly; the return is absolutely theoretical.

Action of Bromide of Aluminium on Bromide of Ethylene, CH_2Br-CH_2Br.—A. Mouneyrat.—The author concludes from his experiments that bromide of aluminium also possesses the property of creating *ethylenic chains*, and can thus be a bromidising agent.

The Aromatic Diurethanes of Piperazine.—P. Cazeneuve and M. Moreau.—The authors thought that piperazine, which is a diazine possessing two NH in the nucleus, would act like two molecules of piperidine coupled. As a matter of fact they obtained with the phenolic carbonates bodies of the form—

$$CO\begin{matrix}<\\>\end{matrix}N<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}>N\begin{matrix}<\\>\end{matrix}CO\ ;\quad \begin{matrix}OR\\RO\end{matrix}$$

R being an aromatic radical. These are true piperazinic diurethanes.

Aromatic Urethanes of Conicine.—P. Cazeneuve and H. Moreau.—The authors have prepared three urethanes of conicine, viz., the phenylic, the gaiacolic, and the α and β naphtholic. The gaiacolic and naphtholic derivatives have undoubtedly a rotatory power, but not enough was prepared to enable this to be measured.

Action of Chloride of Titanium, $TiCl_4$, on some Organic Compounds.—M. Kling.—The action of $TiCl_4$ on pure aniline gives only fuchsine, leaving on calcination notable quantities of TiO_2. By its action on anisol, at first in the cold and then at 200° in a sealed tube, there was an abundant disengagement of CH_3Cl, and a crystalline residue of ortho-titanate of phenyl was left.

Differential Reaction of Creosote and Gaiacols.—H. Fonzes-Diacon.—A scale of colours varying from a yellow-orange to a yellowish-green can be obtained similar to that described by M. Adrian, by treating, say, 10 c.c. of solutions made by dissolving 10 drops of gaiacols and creosotes in a litre of distilled water, by 2 c.c. of a solution of 0·5 grm. per 1000 of sulphate of copper, and 1 c.c. of a solution of 4 per 1000 of cyanide of potassium.

Journal de Pharmacie et de Chimie, Series 6, vol. vii., No. 9.

The Estimation of Succinic Acid in the presence of Tartaric and Lactic Acids.—MM. Bordas, Joulin, and de Raczkowski.—(See p. 18).

The Activity of the Pancreatines.—Eug. Choay.—In the course of some recent work the author had occasion to prepare an aqueous extract of the pancreas of a pig. It occurred to him to make comparative experiments with it and commercial pancreatine, and he found the proteolytic power of the extract far superior to that of the commercial article of a brand very well known in pharmacy. The same was observed with regard to the power of liquefying starch paste. Other experiments were made on its action on fibrine, starch, and fat, and the conclusions drawn are: 1, that it is of great importance to assay all pancreatines; 2, that the aqueous extract of the pancreas concentrated in vacuo at a low temperature is an excellent preparation; 3, that pancreatine prepared carefully according to the Codex has the same activity as the aqueous extract on proteic and amylaceous materials. They only differ from that prepared *in vacuo* in that their power of saponification is greater.

Note on Salicylate of Methyl.—M. Adrian.—In view of the different boiling points given by different writers the author undertook some fractional distillations on two samples, one essence of winter-green and the other salicylate of methyl, and found that pure salicylate of methyl distils over between 220° and 223°, and that its density at 15° is from 1·15 to 1·20. It is nearly insoluble in water, but dissolves easily in alcohol and in ether. It takes a violet colour on the addition of perchloride of iron in a dilute aqueous solution. This ether is a true acid, and combines with potash, forming a crystalline salt. If we place one volume of methyl-salicylic ether in a stoppered flask with five or six volumes of concentrated ammonia, the ether disappears after a time; on the liquor being evaporated and the residue distilled, we obtain a yellow mass which crystallises in needles by dissolving in boiling water. This substance is salicylamide, which by the action of acids regenerates the ammonia in the form of a salt, and forms salicylic acid. The density and boiling point of salicylate of methyl are important indications of its purity; it may contain non-etherised methylic alcohol if the product is not properly washed, or methylic or ethylic alcohol added by fraud. The presence of either of these foreign bodies will notably lower the density and the initial point of distillation; a simple washing with distilled water will, however, suffice to purify the

salicylate. This body may also be adulterated with a fixed oil, but the density will again be lowered, and, after distilling at 230°, a residue will be left, which will give off characteristic vapours of acrolein on being heated to a higher temperature.

MISCELLANEOUS.

South African Industrial and Arts Exhibition.—An Exhibition of the products, manufactures, and mineral wealth of the various States and Colonies of South Africa, together with the varied manufactures and merchandise which are or might be imported from other countries, will be held at Grahamstown in December, 1898. The recent great extensions of the South African railways will doubtless help this Exhibition to be even a greater success than the one held in 1887-88. Attention is directed to the fact that this Exhibition may serve to form the nucleus of a collection of articles illustrative of South African products and industries, to be sent to the Paris Exhibition of 1900. The diamond and gold industries will be specially represented, and the Rhodesian Government will do their utmost to show the latent wealth and resources of this new country. Exhibits from abroad will be brought from any port in the Colony, in bond, carriage free, and will not be subject to duty unless sold. It is expected that the steam-ship companies will carry exhibits from abroad at reduced rates. Diplomas and medals will be awarded to successful exhibitors in every department. The Exhibition will be opened on Thursday, December 15th, 1898, and will be closed on Saturday, January 21st, 1899. It will be divided into five principal groups:—A. Raw Materials; B. Manufactures; C. Mining and Machinery; D. Natural History and Science; E. Fine Arts. These again will be subdivided into a number of sections and groups. Schedules of application for space may be had from the Secretary, Mr. G. B. Wedderburn. These must be filled up and returned by October 31st. Messrs. William Savage and Sons, Blomfield House, London Wall, E.C., have been appointed the Agents in London, and will supply all further information.

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THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2018.

ON POLONIUM: A NEW RADIO-ACTIVE SUBSTANCE CONTAINED IN PITCHBLENDE.

By P. CURIE and Mdme. S. CURIE.

CERTAIN minerals containing uranium and thorium (pitchblende, chalcolite, uranite) are very active from the point of view of the emission of the new rays described by M. Becquerel. In a previous work one of us showed that their activity is even greater than that of uranium and thorium, and expressed the opinion that this effect was due to the presence of another very active substance in these minerals, though in very small quantities (Mdme. S. Curie, *Comptes Rendus*, cxxvi., p. 1101).

The continued study of the compounds of uranium and of thorium have shown, as a matter of fact, that the property of emitting rays which make the air a conductor, and which also act on photographic plates, is a specific property of uranium and thorium, both of these being present in all these compounds, but this characteristic is weaker as the proportion of the active metal present in the mineral is smaller. The physical condition of the metal seems to be of an altogether secondary importance. Various experiments have shown that the conditions of mixture of these substances does not seem to have any effect except in varying the proportion of the active bodies, and the absorption produced by the inert matter. Certain causes (such as the presence of impurities), which act in such a powerful manner on phosphorescence and fluorescence, are in this case entirely inert. From this fact it appears very probable that if certain minerals are more active than are uranium and thorium, it is due to the fact that they contain a substance more active than either of these two metals.

We have endeavoured to isolate this substance from pitchblende, and experiment has confirmed our previous ideas.

Our chemical researches have been constantly guided by the confirmation of the radiant activity of the products separated by each operation. Every product was in turn placed on one of the plates of the condenser, and the conductivity acquired by the interposed air was measured by means of an electrometer and the apparatus already described in a previous paper. We have thus not only an indication, but an actual scale which shows the richness of the body in degrees of the active substance.

The pitchblende which we analysed was about twice and a half more active than the uranium used in our plate apparatus. We have attacked it with acids, and treated the solution formed with sulphuretted hydrogen. The uranium and the thorium remained in solution. We also noted the following facts:—

The precipitated sulphides contain a very active substance besides lead, bismuth, copper, arsenic, and antimony.

This substance was perfectly insoluble in sulphide of ammonium, which separated it from the arsenic and antimony.

The sulphides insoluble in sulphide of ammonium were dissolved in nitric acid; the active substance can be partially separated from the lead by means of sulphuric acid. By exhausting the sulphate of lead by means of dilute sulphuric acid we can to a great extent dissolve the active material which has been carried down with the lead.

This substance, now in solution with bismuth and copper, is completely precipitated by ammonium, which separates it from the copper.

Finally, this active body remains, in company with bismuth.

We have not yet succeeded in finding any method of separating these two bodies by the wet way. We have, however, succeeded in making partial separations based on the following facts:—

In the solution of the sulphides in nitric acid, the easiest parts to dissolve are the least active. In the precipitation of the salts by water the precipitated portions are much the most active.

We have also observed that by heating pitchblende we obtained a very active body by sublimation. This observation has led us to a process of separation founded on the different volatility of the active sulphide and the sulphide of bismuth. The sulphides are heated in vacuo in a Bohemian glass tube to about 700°. The active substance is deposited in the form of a black film in that portion of the tube which is between 250°—300° temperature, while the sulphide of bismuth remains in the warmer part of the tube.

By carrying out these various operations we obtain products of greater and greater activity.

Finally, we obtained a body of which the activity is 400 times greater than that of uranium.

We have searched among all known elements for any with such activity. We have examined the compounds of nearly all the similar bodies; thanks to the kindness of many chemists we have had the use of samples of the most rare bodies. Uranium and thorium alone are practically active: tantalum is so perhaps to a very feeble extent.

We therefore believe that the substance we have isolated from pitchblende contains a hitherto unknown metal, very similar to bismuth in its analytical properties.

If the existence of this new metal is confirmed we propose for it the name *Polonium*, after the native country of one of us.

M. Demarçay has been kind enough to examine the spectrum of the body we have found, but he has not been able to distinguish any characteristic line except those due to impurities.

This fact does not favour the idea of the existence of a new metal. However, M. Demarçay reminds us that uranium, thorium, and tantalum give peculiar spectra, formed of innumerable fine and difficultly seen lines. (M. Demarçay, "Spectres Electriques," 1895).

May we be permitted to add, that if the existence of a new simple body is confirmed, this discovery will be entirely due to the new method of investigation given to us by the rays discovered by M. Becquerel.—*Comptes Rendus*, vol. cxxvii., No. 3, July 18, 1898.

ON THE MIXED HALOGEN SALTS OF LEAD.

By V. THOMAS.

IF the history of the halogen salts of lead is now familiar to us the same cannot be said of the history of the mixed salts, combinations of the chloride and iodide, the chloride and bromide, the bromide and iodide, in spite of the number of chemists who have taken up the study.

It is the study of this question that I have recently been engaged on.

Chloroiodides of Lead.—The chloroiodides of lead may be formed:—

1. By dissolving an iodide in hydrochloric acid.
2. By the mixture of an alkaline iodide with chloride of lead.
3. By the solution of iodide of lead in an alkaline chloride.

4. By boiling a solution of chloride of lead with iodide of lead.

These methods have been successively applied with more or lese success by Laboure, Dietzel, Poggiale, Engelhardt, Miss Field, and by Herty.

Laboure (*Journ. de Pharm. et de Chim.*, Series 3, vol. iv., p. 328), by treating iodide of lead with boiling hydrochloric acid, obtained a red solution, which on cooling produced prismatic crystals. But the author did not submit these crystals to analysis; the experiment was afterwards repeated by Dietzel (*Dingl. Polyt. Journ.*, vol. cxc., p. 41). This chemist gave it the formula PbICl.

In the year 1845 Poggiale (*Comptes Rendus*, vol. xx., p. 1180), described several double haloids, and in particular a chloroiodide of lead, which he obtained by treating a solution of chloride of lead with iodide of sodium, or by dissolving iodide of lead in chloride of ammonium. Poggiale gave it the formula $PbI_2,2PbCl_2$. It is to be regretted that the original memoir did not mention the relative proportions of the salts necessary to obtain this compound.

Engelhardt (*Journ. f. Prakt. Chim.*, vol. lxvii., p. 293; 1856), in a long paper on the action of metallic chlorides on iodide of lead, again took up the question. He first of all studied the action of iodide of lead on the chloride. According to this writer, by boiling a certain quantity of iodide of lead in water, in the presence of an excess of chloride of lead, the iodide of lead is rapidly transformed into a yellow powder. The liquor, when left to cool, deposits white crystals in the form of needles; these crystals are nothing else but the chloride. As for the yellow powder, by boiling it up again with water, which partially dissolves it, we obtain a solution which on cooling gives very good crystals of a yellow colour, very much in the form of needles. The residue again treated with water leaves another residue, and also gives a solution which, under favourable circumstances, deposits small crystals analogous to those already mentioned, but of a much deeper colour.

If instead of treating a mixture of the iodide and the chloride by water, we mix the warm solution of these two salts we arrive at the same results as before, which are:—

1. The percentage of lead in the first compound is 68·93.

2. The proportion of lead present diminishes as the number of treatments by water increases. The crystals isolated the second time contain 59·35 per cent of lead. Engelhardt has slightly varied the conditions of this experiment. Instead of successively treating the different yellow residues with boiling water, in a second series of experiments he took up the residues with the corresponding filtrate from which the yellow crystals had already been allowed to separate by cooling. Under these conditions the estimations of the lead gave him figures intermediate between those already mentioned; that is to say, about 63·5 per cent.

To obtain similar results it is necessary to work not only in the presence of an excess of chloride of lead, but with solutions saturated with this salt.

When the iodide is in excess we obtain compounds in which the proportion of lead present is comprised between the limits Pb = 56·09 and Pb = 74·5.

The proportion of lead becomes less as the quantity of chloride used diminishes.

Engelhardt evidently considered these compounds as mixtures in varying proportions, since he proposed to include them all in the general formula:—PbI_xCl_y, a formula in which $x + y = 2$ with $x < 1$ and $y > 1$.

Instead of elucidating this question the work of the German chemist appears, on the contrary, more calculated to make the matter more indecisive than it was before he took the subject up.*

* I would here remark that the original paper did not contain the estimation of the halogen, either as a whole or separated (Cl + I or Cl.I), as far as it concerns the reciprocal action of the chloride and the iodide of lead.

Miss Field (Chem. News, vol. lxvii., p. 157, 1893), has examined the mixed salts of lead over again, and shows that by heating together—

I.

PbI_2	1 grm.
AmCl	6 „
H_2O	50 „

a well crystallised chloroiodide was obtained. By boiling the mixture a yellowish powder is formed consisting principally of chloride and oxychloride with traces of iodide. By filtering the solution and leaving to stand till cold small green crystals are soon deposited. This filtrate contains chloride of lead and potassium, but no iodide. If these proportions are not exactly adhered to we get mixtures of chloride and iodide.

The author gives these green crystals, dried at 100°, the formula $PbICl + \frac{1}{2}H_2O$. By varying the proportions of the salts used Miss Field has succeeded in obtaining other compounds. For example, by boiling up—

II.

KI	1 grm.
$PbCl_2$	5 „
H_2O	250 „

and filtering the solution, we notice the formation of small green crystals which dissolve in water without decomposition, and which do not change colour when heated to 100°. According to the author it is difficult to obtain them in a state of purity, as they always entangle in them a small quantity of chloride and iodide. These crystals correspond to the two formulæ $3PbCl_2PbI_2$ and $5PbCl_2PbI_2$, no doubt according to the method of preparation used, but Miss Field does not show how we can prepare one or the other of them at will.

Finally, M. Herty (*Am. Chem. Journ.*, vol. xviii., p. 290), in quite a recent paper, has repeated Miss Field's experiments, and he concludes most decisively, although his conclusions do not appear according to his paper unassailable, that these compounds, until now regarded by him as chloroiodides of lead, are in reality nothing more than isomorphous mixtures of chloride and iodide.

I shall now examine successively the different methods proposed for the preparation of chloroiodides.

The Action of Hydrochloric Acid on Iodide of Lead.—The action of boiling concentrated hydrochloric acid on iodide of lead always gives rise to the formation of a corresponding chloroiodide having the formula PbICl, as shown by Dietzel. According to the length of the reaction and the relative proportions of the salt of lead and the acid present, so we obtain it in a state of purity, or mixed with iodide of lead. Analysis gives almost theoretical figures, although the figure for Cl is sometimes 0·5 per cent higher than the figure given by theory, viz.—theory, 9·63; found, 10·13.

This slight error with regard to the chlorine has made me suspect that the chloroiodide might in certain cases contain small quantities of chlorine as an impurity. This error is frequent if the estimation is made on large crystals, but if these are pulverised and the powder again dried on a porous plate, the preparation of chlorine found is almost exactly what is demanded by theory. Found, 9·59; calculated, 9·63.

The quantity of iodine found, no matter what the chlorine may be, is the theoretical amount: found, 34·42; calculated, 34·47. The same is the case with the lead; found, 56·01; calculated, 55·90.

These analytical results do not allow us to consider the presence of chloride of lead as an impurity. Further, we could not explain the presence of chloride of lead in the chloroiodide, even in a very minute quantity, as this body could only be formed by a previous decomposition of the iodide of lead, and must, therefore, *a fortiori*, be produced by the ebullition or the chloroiodide with the hydrochloric acid. Now the chloroiodide thus treated does not appear to undergo any modification, even after some considerable

time. It thus follows that the slight excess of chlorine sometimes shown by analysis is caused by a small quantity of hydrochloric acid being entangled in the crystals themselves.

To obtain the chloroiodide free from iodide of lead, it is necessary to work in the presence of a large excess of hydrochloric acid and also to keep the solution boiling for a considerable time; without this precaution, the iodide will be found to deposit the first on cooling, then only after some moments the chloroiodide appears, with a more or less abundant quantity of PbI_2.

The solution of chloride of lead in hydriodic acid does not enable us to prepare the chloroiodide, for it is a long known fact that hydriodic acid completely displaces hydrochloric acid from its salt of lead.

Reciprocal Actions of Alkaline Chlorides or Iodides with the Haloid Salts of Lead.—If we cause iodide of lead to react on a chloride, or an iodide on a chloride of lead, the question is entirely the same. In fact we find ourselves, by double decompositions, in the presence of a chloride and iodide of lead. The result I have achieved is extremely simple; I have never been able to prepare anything but a single compound, the chloroiodide, PbICl, either pure or more or less adulterated with chloride of lead. In particular, I repeated the experiments of Miss Field with the greatest care. Starting from the first system:—

I.

PbI_2	1 grm.
AmCl	6 „
H_2O	50 „

I always and very regularly obtained the body mentioned by this chemist. I would, however, point out that, while Miss Field attributed to the chloroiodide, dried at about 100°, half a molecule of water of crystallisation, I always found this salt anhydrous, as shown by the following analysis by drying in the cold on a porous plate. Found: Pb, 56·05; Cl, 9·22; I, 34·42. Calculated: Pb, 55·90; Cl, 9·63; I, 34·47.

It is this same anhydrous salt that I obtained by the second method:—

II.

KI	1 grm.
$PbCl_2$	5 „
H_2O	250 „

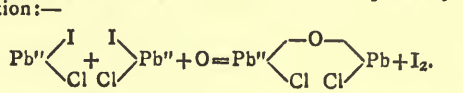
The chloride of lead (5 grms.) was dissolved in 240 c.c. of hot water, to which is added 10 c.c. of a one-tenth solution of iodide of potassium. The addition of iodide of potassium produces first of all a yellow precipitate which dissolves almost immediately, and at the same time deposits greenish crystals. This can further be fractionally crystallised by collecting the precipitate formed at 70°, 60°, 50°, 40°, &c., by successive coolings; it is necessary to go to a relatively low temperature (say 30°) to enable the microscope to reveal a mixture, and for analysis to show an excess of chlorine. The precipitates collected at first, and then at lower temperatures, such as 70°, 60°, 50°, and even 40°, corresponds exactly with the formula PbI.Cl.

Towards 10°, on the contrary, the precipitate is formed of chloride of lead, entirely free from any trace of iodide.

Must we then conclude that, according to the preceding method, it is only possible to produce a single chloroiodide of lead? No; but it seems now to be well proved that the chloroiodide of lead, PbICl, is a very stable compound and is formed with great facility. Other workers of greater experience may *perhaps* have been able to produce compounds differing from this one; but in any case is to be hoped that their chemical existence may be well proved. As for the chloroiodide, PbICl, its existence is proved by the product of oxidation which it is susceptible of forming when treated with peroxide of nitrogen.

I have had occasion to show (*These de Doctorat*, Gautier-Villars, 1897), that the different halogen compounds of lead behave in various manners with the hyponitride. In fact, while at the ordinary temperature the chloride and bromide were not attacked, the iodised compound was completely decomposed with the liberation of iodine and formation of oxide of lead, even at a low temperature. It should therefore be presumed that such a compound as PbICl treated by the hyponitride ought to give rise to the liberation of iodine and the formation of a corresponding oxychloride. It is this that experiment verifies; the displacement of the iodine commences in the cold, but it is necessary, to renew the active surfaces, to raise the temperature sufficiently to cause the sublimation of the iodine.

The decrease in weight observed is that required by the equation:—



Further, the estimation of the chlorine gives 14·14 against the theoretical figure 14·23.

The process which enables us easily to produce Matlockite gives the same facilities for distinguishing the mixtures of the iodides and chlorides, properly called chloroiodides. While the chloroiodides give rise to corresponding oxychlorides, the chlorides and the iodides behave differently. The chlorides are not attacked, and the iodides are transformed into oxides so completely that by treating the residue from the oxidation with warm water we can completely exhaust it, leaving a residue of pure oxide of lead.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 12.

AMMONIUM SELENIDE.

By VICTOR LENHER and EDGAR F. SMITH.

By bringing ammonia and hydrogen selenide together Bineau (*Ann. Chim. Phys.*, 2, 67, 227), claims to have prepared ammonium selenide. His product was a white, crystalline solid, which was readily decomposed by water in the presence of air. No mention occurs anywhere that this compound was ever obtained by crystallisation from solution, hence it may be of interest to note that when prepared by the latter method it crystallises in black, anhydrous, orthorhombic prisms. Peculiar conditions, however, seem necessary for its formation. Thus, in attempting to make ammonium selenomolybdate it was observed that when an ammoniacal solution of ammonium molybdate was saturated with hydrogen selenide gas a dark-red coloured solution resulted, which yielded the black crystals of ammonium selenide upon careful evaporation. The solution contained five grms. of ammonium molybdate in 50 c.c. of water, to which 20 c.c. of the strongest ammonia water had been added. The solution was saturated with hydrogen selenide gas. The resulting liquid, deep red in colour, was concentrated in a vacuum over sulphuric acid. The final residue consisted of ammonium molybdate, metallic selenium, and well-defined, black, orthorhombic crystals. The latter were separated as completely as possible from the selenium, and extracted for several days with pure carbon disulphide. The crystalline mass, purified as far as possible in this manner, proved to be stable in the air, and dissolved readily in water to a dark red coloured solution. The latter, when freshly made, precipitated selenides from neutral or alkaline solutions of metallic salts. On exposure to the air, however, the solution of the salt suffered decomposition with the separation of black selenium. An excess of ammonia seems not to prevent the change.

The analysis gave as follows:—

1. 0·3051 grm. of substance gave 0·2137 grm. selenium = 70·04 per cent selenium.

2. 0·2031 grm. of substance gave 0·1418 grm. of selenium = 69·81 per cent selenium.

Ammonium.

3. 0·2012 grm. of substance gave 0·0603 grm. of ammonium = 29·97 per cent ammonium.

4. 0·3036 grm. of substance gave 0·9918 grm. of ammonium = 30·24 per cent ammonium.

The discrepancy between the found and calculated percentages is due to metallic selenium, which adhered to the ammonium selenide crystals. The salt was distilled with sodium hydroxide in determining the ammonium content. The liberated ammonia was absorbed by standard hydrochloric acid, the excess of the latter being titrated with standardised alkali.

In estimating the selenium a weighed quantity of the salt was dissolved in water containing a little sodium hydroxide. An excess of hydroxylamine* hydrochloride was added to this solution, from which the selenium separated completely after boiling several minutes. It was then transferred to a weighed Gooch filter, washed with water, and dried at 105° for one hour. This method is far superior to the usual course of precipitating selenium by means of sulphurious acid.

The ammoniacal molybdate solution of the strength given in the preceding lines is the only solution from which the black crystals were obtained. Under these conditions the salt was always found, but with molybdate solutions of greater dilution or with such as contained arsenic acid or tungstic acid, evaporation showed nothing but metallic selenium.—*Journal of the American Chemical Society*, xx., No. 4.

SOME PROPERTIES OF ZIRCONIUM DIOXIDE.

By F. P. VENABLE and A. W. BELDEN.

THERE are so many misstatements as to the properties of zirconia in the literature of chemistry that we think it well to publish the results of our study of this body.

1. *Specific Gravity.*—The following values have been given:—4·30 (Berzelius), 4·90 (Berlin), 5·50 (Sjögren), and 5·45 (Hermann). Our determinations were made with quite pure material, and yielded as a mean 5·489.

2. *Solubility.*—The strongly ignited zirconia is practically insoluble in all acids except hydrofluoric. In this it is readily soluble on heating. If soda is present along with the zirconia, as sodium zirconate, the mass is not dissolved, probably owing to the formation of sodium zirconium fluoride. The statement is frequently met with that zirconia is soluble in sulphuric acid. This is based upon observations of Berzelius, and his directions are that the zirconia must be finely powdered and heated with a mixture of two parts sulphuric acid and one part water until the sulphuric acid volatilises. Our experiments would show that it is quite insoluble in concentrated sulphuric acid, and when the directions of Berzelius are followed out this dilute acid dissolves only 6·72 parts to the 1000 parts of acid. Neither concentrated nor dilute hydrochloric acid, nor nitric acid, seem to have much action upon it.

Prolonged heating with sodium carbonate effects very little change in zirconia. It is only sparingly dissolved. Berzelius must have made use of a carbonate carrying some hydroxide in the experiments in which he speaks of dissolving the zirconia by means of sodium carbonate.

Again, ½ a grm. of zirconia (finely powdered) was fused for nine hours with 20 grms. of microcosmic salt. The zirconia did not apparently enter into the fusion, nor could the formation of crystals be observed as has been maintained. The same results were observed in a similar experiment with borax.

3. *Zirconium Hydroxide.*—The statement is made in Dammer's "Handbook" (i., 619) that of the two possible hydroxides only $ZrO(OH)_2$ is known, and that, further, numerous pyrohydrates are known whose contents of water lie between this and the anhydride. This is based upon the work of G. J. Bruch (*Jahresber.*, 1854, 729), who described a meta-zirconic acid, $ZrO(OH)_2$, prepared as a white, voluminous, almost gelatinous precipitate, by precipitating a solution of a salt of zirconium with ammonia.

In the following experiments this precipitate, gotten with ammonium hydroxide, was washed free of ammonia, then placed in a Gooch crucible and washed about twelve times with alcohol (95 per cent). It was then washed with ether. After weighing the crucible it was heated strongly, and the loss of water was 26·50 per cent. In a second experiment the zirconium hydroxide precipitate was pressed between filter-paper, placed in a Gooch crucible, and washed with petroleum ether until there was no further loss of weight. This washing was done in an atmosphere free from carbon dioxide. Afterwards the crucible was strongly heated. The loss of water was 26·19 per cent. A third experiment carried out in a similar manner yielded also 26·30 per cent. Other experiments gave losses of 25·97 per cent and 27·21 per cent. The percentage of water in $Zr(OH)_4$ is 22·69. It would therefore seem that treatment with petroleum ether brought the precipitate very nearly down to the composition $Zr(OH)_4$. In using alcohol and ether there seemed to be no definite limit to the removal of water, and hence in several experiments final constant weights were not obtained. Two experiments gave respectively 11·11 and 9·45 per cent of water. The percentage in $ZrO(OH)_2$ is 12·80.

A specific gravity determination of the hydroxide containing 25·97 per cent of water gave 3·25.

4. *Solubility of the Hydroxide.*—The statement of Bruch, that this substance is soluble in 5000 parts of water, and turns litmus paper blue and turmeric paper orange yellow, is cited by several authors. This is manifestly an error. The alkaline reaction observed was doubtless due to the ammonia which it so persistently retains when ammonium hydroxide is used in the precipitation. Bailey and others have noted how prolonged the washings must be to free the hydroxide from ammonia. Experiments were carefully carried out to test this point, but we failed to detect in the pure hydroxide any alkaline reaction or any appreciable solubility in pure water. Certainly it is less than the figure given by Bruch.

The solubility of the cold precipitated hydroxide in acids is as follows:—It is very readily soluble in concentrated and dilute hydrochloric acid (which is the best solvent for it), in hydrofluoric acid, and in hydrobromic acid. It is very sparingly dissolved by hydriodic acid. Concentrated and dilute nitric acid dissolve it easily.

Among the organic acids it was found that oxalic acid was the best solvent, dissolving it nearly as well as the mineral acids. Saturated solutions of tartaric and citric acids dissolved less than 1:1,000 and glacial acetic acid also dissolved very little.

If the zirconium hydroxide is precipitated from a hot solution it is much less soluble in the dilute acids. Thus dilute hydrochloric or dilute nitric acid will dissolve only about 1:100 and dilute oxalic acid dissolves only about half as much. If the precipitate, however, stands for some days in contact with the acid it is dissolved to about the same extent as when precipitated cold.

As to the solubility in basic substances, ammonia (sp. gr. 0·90) does not seem to appreciably dissolve it, but when diluted (sp. gr. 0·96) there is dissolved about 1:10,000 parts of ammonia. Clarke (*Journ. Amer. Chem. Soc.*, xviii., 434), has shown the solubility in potassium hydroxide, and in sodium hydroxide to be as follows:—

							Grms.
50	per cent	KOH	solution	dissolved	per c.c.	..	0·00233
33	"	"	"	"	"	..	0·00097
25	"	"	"	"	"	..	0·00075
12	"	"	"	"	"	..	0·00009
33	"	NaOH	"	"	"	..	0·00245
25	"	"	"	"	"	..	0·0012
12	"	"	"	"	"	..	0·0005

* Privately communicated by Dr. H. F. Keller.

Certain salts of ammonia exert quite a solvent action. Thus a saturated ammonium carbonate solution will dissolve about 1 : 100, and a solution of ammonium tartrate rendered strongly ammoniacal has a somewhat smaller solvent action.

5. *Absorption of Carbon Dioxide.*—Zirconium hydroxide shows a decided tendency to absorb carbon dioxide. This may be observed on exposing the moist precipitate to the air or on prolonged heating at a low temperature (100°—150°) over an ordinary burner. Such a mass will gain very noticeably in weight. The extent of this absorption of carbon dioxide was tested as follows: About two grms. of the moist hydroxide were placed in a porcelain boat in a tube and pure carbon dioxide passed over it for some twenty-five or thirty hours. At the end of this time the hydroxide had contracted into small, hard, horn-like particles and no further change was observable. Purified air was next passed over these particles for eighteen or twenty hours, and the carbon dioxide coming off was caught in a barium hydroxide solution and determined. Then the particles were heated and the carbon dioxide was caught by a fresh solution of barium hydroxide. It was found that about one-third of the carbon dioxide which had been absorbed came off without heating. As no distinct point could be observed at which this carbon dioxide ceased coming off (no clear line of demarcation between that lost at ordinary temperatures and that lost on heating), no inferences were drawn, and the carbon dioxide was all reported together. The percentages of carbon dioxide absorbed were 16·42, 5·72, and 7·05. These show a wide variation, and can scarcely be taken as showing more than the fact that considerable amounts of the gas are absorbed with the formation of basic carbonates. The basic carbonate, $Zr(CO_3)_2.2Zr(OH)_4$, contains 16·68 per cent of carbon dioxide, and $Zr(CO_3)_2.6Zr(OH)_4$ contains 7·55 per cent, and $Zr(CO_3)_2.8Zr(OH)_4$ contains 5·96 per cent.

This experiment was varied somewhat by suspending the zirconium hydroxide in water and passing carbon dioxide through the water. This gave 6·73 and 6·00 as the percentages of carbon dioxide absorbed in two separate trials.—*Journal of the American Chemical Society*, vol. xx., No. 4.

FURTHER SEPARATIONS OF ALUMINUM BY HYDROCHLORIC ACID.*

By FRANKE STUART HAVENS.

In former papers from this laboratory (Gooch and Havens, *Am. Journ. Sci.*, ii., 416; Havens, *Ibid.*, iv., p. 111), methods have been described for the separation of aluminum from ferric iron, and from beryllium, based on the insolubility of the hydrous aluminum chloride in a mixture of equal parts of aqueous hydrochloric acid and ether saturated with hydrochloric acid gas; the ferric and beryllium chlorides being exceedingly soluble in this mixture.

It was the purpose of the investigation herein described to discover how far this process could be extended, with certain modifications, to cover the separation of aluminum from such other metals as might occur with it, either in artificially prepared alloys or in naturally-occurring compounds.

The aluminum used in all the following experiments was in the form of a solution of the chloride. This chloride was purified, as previously described (*loc. cit.*), from iron by precipitation with hydrochloric acid, and from the alkalis by precipitation as the hydroxide and continued washing with water until the washings gave no test with silver nitrate. The hydroxide thus obtained was dissolved in hot hydrochloric acid to get it into the form of the chloride. The chloride solution was standardised by precipitating weighed portions with ammonia and weighing as the oxide.

Separation of Aluminum from Zinc.

A solution of pure zinc chloride made by dissolving metallic zinc, free from impurities, in hydrochloric acid, is not precipitated when treated with an equal volume of ether and saturated with hydrochloric acid gas.

To prepare a definite zinc salt free from traces of the alkalis which would be precipitated with the aluminum by strong hydrochloric acid, pure metallic zinc was dissolved in hydrochloric acid, the dilute solution precipitated with ammonium carbonate, and the resulting carbonate ignited to a constant weight as zinc oxide. This oxide dissolved in hydrochloric acid gave a pure chloride.

The aluminum in all these experiments was determined in the following manner:—Portions of the prepared solution of aluminum chloride were weighed in a small beaker, weighed portions of zinc oxide added and sufficient aqueous hydrochloric acid to dissolve it. The beaker was then cooled by immersion in an inverted bell-jar supplied with running water by means of inlet and outlet tubes, and a current of gaseous hydrochloric acid (generated by the gradual addition of sulphuric acid to a mixture of hydrochloric acid and salt) passed through the solution in the beaker to complete saturation. Ether was added in volume equal to that of the original solution, and the whole again saturated with hydrochloric acid gas. The crystalline chloride precipitated was caught on asbestos in a filter crucible, washed with a previously prepared solution of equal parts of ether and hydrochloric acid, saturated with hydrochloric acid gas, dried for half an hour at 150—180° C., covered with a layer of pure mercury oxide, heated gently over a low flame under a ventilating hood, ignited over the blast, and weighed as the oxide. The results show that aluminum can be determined with reasonable accuracy in the presence of a pure zinc salt.

The zinc can be determined, after the evaporation of the strong acid filtrate, by any of the well known methods. It was found, however, that after thorough conversion to the nitrate by repeated evaporation with nitric acid the salt could be ignited directly to the oxide with satisfactory results. This is shown clearly in Table I. (Experiments 3 to 5). In Experiments 3 and 4, zinc oxide was dissolved in nitric acid and the nitrate ignited again to the oxide. In Experiment 5, the zinc oxide was first dissolved in hydrochloric acid and the chloride thus obtained was converted to the nitrate by evaporating the solution (5 c.m.³) with nitric acid (2 c.m.³), treating the residue with nitric acid (2 c.m.³), and evaporating to dryness.

In Table I. (Experiments 6—11) are given the results of experiments in which both the aluminum and zinc were determined—the former, as described, by precipitating as the hydrous chloride and weighing as the oxide, and the latter by carefully evaporating the strongly acid filtrate (best with a small current of air playing on the surface of the liquid to avoid spattering due to the too violent evolution of the ether and gaseous acid), and finally converting the chloride through the nitrate into the oxide. It is, of course, absolutely necessary that the treatment with nitric acid shall be thorough, so that no zinc chloride may remain to volatilise when the residue is ignited. On account of the danger to platinum from the aqua regia generated by the action of nitric acid on zinc chloride, the evaporations of the filtrates from the aluminum chloride and the treatment with nitric acid were carried on in porcelain, and the residual nitrate was transferred to a small crucible for ignition. In this process the porcelain was evidently attacked somewhat, so that the residual nitrate was slightly contaminated with material from the large porcelain dish. This fact accounts for the high results given in the first column of errors. However, on introducing a correction (0·0020) found by carrying

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vi., 1898.

TABLE I.

	Al_2O_3 taken as the chloride.	Al_2O_3 found.	Error.	ZnO taken.	ZnO found.	Error.	Error corrected.	Final vol.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	C.m.³.
1.	0·0562	0·0562	0·0000	0·1110	—	—	—	—
2.	0·0580	0·0577	0·0003 −	0·1034	—	—	—	—
3.	—	—	—	0·1019	0·1016	0·0003 −	—	—
4.	—	—	—	0·1010	0·1007	0·0003 −	—	—
5.	—	—	—	0·1100	0·1095	0·0005 −	—	—
6.	0·0572	0·0572	0·0000	0·1014	0·1027	0·0013 +	0·0007 −	12
7.	0·0563	0·0550	0·0013 −	0·1026	0·1038	0·0012 +	0·0008 −	16
8.	0·0577	0·0576	0·0001 −	0·1000	0·1014	0·0014 +	0·0006 −	16
9.	0·0559	0·0558	0·0001 −	0·1020	0·1035	0·0015 +	0·0005 −	16
10.	0·0563	0·0556	0·0007 −	0·2024	0·2046	0·0022 +	0·0002 +	20
11.	0·1111	0·1107	0·0004 −	0·2092	0·2116	0·0024 +	0·0004 +	20

TABLE II.

	Al_2O_3 taken as the chloride.	Al_2O_3 found.	Error.	CuO taken.	CuO found.	Error.	$HgCl_2$ taken.	Bi_2O_3 taken.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·0576	0·0571	0·0005 −	0·0500	—	—	—	—
2.	0·0561	0·0557	0·0004 −	0·0400	—	—	—	—
3.	0·0570	0·0574	0·0004 +	—	—	—	0·1000	—
4.	0·0548	0·0557	0·0009 +	—	—	—	0·1000	—
5.	0·0565	0·0571	0·0006 +	—	—	—	—	0·1000
6.	0·0576	0·0577	0·0001 +	—	—	—	—	0·2000
7.	—	—	—	0·0437	0·0432	0·0005 −	—	—
8.	—	—	—	0·0359	0·0359	0·0000	—	—
9.	—	—	—	0·0345	0·0340	0·0005 −	—	—
10.	0·0558	0·0545	0·0013 −	0·0319	0·0324	0·0005 +	—	—
11.	0·0538	0·0536	0·0002 −	0·0343	0·0356	0·0013 +	—	—
12.	0·0566	0·0562	0·0004 −	0·0337	0·0349	0·0012 +	—	—
13.	0·0577	0·0575	0·0002 −	0·0651	0·0644	0·0007 −	—	—

through the process in blank with the quantities of reagents employed in the regular process, the results on zinc, slightly deficient, agree closely with those obtained (Experiments 3—5, Table I.) where the zinc nitrate was converted directly to the oxide without the previous evaporation in porcelain of a large volume of strongly acid liquid. The errors thus corrected stand in another column of the table.

These results show clearly that aluminum and zinc may be separated from one another by the action of hydrochloric acid gas in aqueous ethereal solution with a reasonable degree of accuracy.

Separation of Aluminum from Copper, Mercury, and Bismuth.

The separation of aluminum from copper, mercury, and bismuth does not differ materially from the separation of aluminum and zinc. Aluminum chloride is precipitated quantitatively in the presence of pure salts of these elements, as shown in experiments of Table II.

In determining the copper in the acid filtrate it was found advantageous to weigh as the oxide, but to arrive at that condition through the sulphate rather than through the nitrate (which was the transition salt in the case of zinc), as this process can be carried on safely in platinum.

In Table II. (Experiments 10 to 13) are given results of experiments in which the aluminum was determined as previously described by precipitation as the hydrous chloride and conversion to the oxide, the acid filtrate was evaporated in platinum and the copper determined by treating the residue with a few drops of strong sulphuric acid, heating gently to drive off the excess of sulphuric acid, and then igniting the sulphate to the oxide at a red heat. That the copper sulphate is converted to the oxide by ignition at a red heat over a Bunsen burner is shown in Experiments 7 to 9 of Table II.

In conclusion, the author wishes to thank Professor Gooch, under whose direction this work has been carried on, for his kind suggestions and advice.

ACTION OF SULPHUR MONOCHLORIDE UPON MINERALS.

By EDGAR F. SMITH.

SULPHUR monochloride has frequently been applied in organic chemistry in the synthesis of various bodies, and the results obtained by the employment of this reagent have invariably had great attraction and interest for the investigator. There are, however, other directions in which the same reagent may be followed with equal interest; *e.g.*, in the action upon the natural products furnished by the mineral world. To illustrate, mention may be made of the behaviour of such substances as arsenopyrite, chalcopyrite, pyrite, and marcasite with the reagent in question. Finely divided arsenopyrite and sulphur monochloride were brought together in a glass tube. After slight agitation, action set in, accompanied by the evolution of much heat, and the almost complete decomposition of the mineral. The tube was then freed from air by the introduction of carbon dioxide. It was sealed and heated to about the boiling-point of the sulphur monochloride (139°) for a period of nine hours. On cooling, beautiful olive-green coloured plates or scales separated. After their removal from the tube and separation from the adherent liquid they proved to be deliquescent and readily soluble in water. Their aqueous solution tested with potassium ferrocyanide and silver nitrate showed the presence of iron in the ferric condition, and also of chlorine. In subsequent decompositions the crystals were filtered out, and washed with petroleum ether; then they were dissolved in water and the iron content determined quantitatively by means of stannous chloride. In this manner it was proved that 32·6 per cent of iron was present in the ferric condition in arsenopyrite. This is certainly a confirmation of the work previously carried out in this direction on arsenopyrite by Starke, Shock, and Smith (*Journ. Amer. Chem. Soc.*, xix., 948).

The petroleum ether solution from the ferric chloride

crystals was distilled, the product diluted with water, and tested with hydrogen sulphide, when the arsenic was precipitated. Its quantity was not estimated.

Chalcopyrite treated in a similar manner with sulphur monochloride, was completely decomposed, with the production of ferric and cupric chlorides. Marcasite and pyrite also gave beautiful crystallisations of iron chloride. The decompositions were in both instances complete and the total iron content determined. On the addition of sulphur monochloride to marcasite and pyrite no action was observed in the cold. With chalcopyrite and arsenopyrite the evolution of heat, as already mentioned, was very great, so that the vessel containing them could not be held in the hand. This difference in behaviour evidently indicates a marked difference in the union of the elements concerned. In pyrite and marcasite we deal with iron and sulphur alone and with them there is an absence of marked reactivity, whereas in arsenopyrite and chalcopyrite we have substitution products in which there is perhaps a less intimate union of the sulphur than exists in the pyrite and marcasite. It may be observed here that Brown (*Proc. American Phil. Soc.*, xxxiii., 1894), while working with marcasite, found that it contained its total iron in the ferrous condition, but when this same mineral was dissolved in sulphur monochloride it gave a mass of iron chloride crystals showing the presence of about 41 per cent of iron in the ferric state. This would mean that this reagent undoubtedly acts as an oxidant; that its power is in a large measure due to its chlorine content, so that we may say of sulphur monochloride it is "chlorine in disguise." This view of its action is corroborated by other decompositions which will be presented later. The experiments upon which the preceding statements are based were carried out by Mr. F. W. Moore.

The mineral stibnite dissolved immediately and completely in sulphur monochloride with a violent ebullition and the generation of much heat. When the solution cooled crystals separated. These were collected and heated with water, with the formation of antimony oxychloride. Much heat was also evolved when cinnabarite and sulphur monochloride were mixed. To effect complete decomposition the mixture was heated in a sealed tube. On cooling long needles were observed throughout the liquid. These proved to be mercuric chloride. Chalcocite was also completely decomposed, with the production of a crystalline powder, which on examination was found to be cupric chloride. This is additional evidence of the oxidising character of the solvent employed, and explains the reason for the obtainment of so much ferric chloride when using marcasite, which contains its iron in the ferrous condition. Tetrahedrite, although of a complex nature, yields in the cold to the influence of the sulphur monochloride, and crystals of ferric chloride appeared in a very short time, although to effect the complete decomposition of the mineral it was necessary to heat it with the reagent to 140° C. Sphalerite was not attacked in the cold, and at 150° its decomposition was very slight, but at 250° C. complete solution occurred. On cooling, a mass of anhydrous zinc chloride separated. This was quickly collected and treated with water, when it dissolved with a hissing noise. The zinc in solution equalled 67·5 per cent.

Galenite, furthermore, was not affected in the cold, but at 250° C. was changed completely to lead chloride. Finely divided molybdenite was not attacked in the cold, nor was it entirely broken up after heating to 300° C. Many of these experiments show that, where the sulphur estimation of a sulphide is not desired, this method of decomposing such minerals may be of use in analysis. This is particularly true in the case of tetrahedrite. Mr. C. S. Reeve was kind enough to conduct these experiments for me.

At my suggestion, Mr. E. W. Pierce brought pure, artificial arsenic trisulphide in contact with sulphur monochloride. A violent reaction set in, and much heat was liberated. On repeating the experiment at a temperature of 0°, the reaction took place slowly with the gradual solution of the metallic sulphide and the appearance of a slight residue of sulphur, which disappeared on the addition of more sulphur monochloride. Nothing separated when the liquid was further chilled. Arsenic sulphide was precipitated from the diluted solution on the addition of hydrogen sulphide. The minerals linnæite $(Co,Ni)_3S_4$, millerite (NiS), gersdorffite (NiAsS), and rammelsbergite $(NiAs)_2$, were also fully decomposed by the monochloride on heating the mixture in sealed tubes to 170° C. Metallic chlorides were formed in all instances and separated from the cold solutions. Cobaltite (CoAs), smaltite $(Co(FeNi)As_2)$, and ullmannite (NiSbS), in a finely divided condition, were dissolved by the sulphur monochloride when heated to 180° C. in a sealed tube. These observations were made by Mr. Jos. Cauffman, who also found that rutile in powdered form was decomposed almost completely by the same reagent, with the production of titanium tetrachloride. This behaviour suggested heating the oxides of molybdenum, tungsten, tantalum, and columbium, as well as the minerals wolframite, scheelite, and columbite with the same reagent when all were dissolved, and from the cold solutions beautiful crystalline bodies separated. Some of these have been analysed, while others are yet under examination and will be discussed in a later communication. The indications are that the action of the sulphur monochloride in these substances is both oxidising and substituting. Combinations of the metallic haloids with sulphur monochloride are not produced. In the case of the sulphides and sulpho salts which were investigated, quantitative determinations of the products were only made in a few instances, for there was no question as to the completeness of the decompositions, and the character of the resulting bodies. Upon considering the facts which are here presented, we recognise that with the sulphides of non-metals, for example stibnite, the action is violent, and the decomposition complete. This is also true of arsenopyrite where arsenic probably facilitates the transposition, whereas with marcasite, pyrite, sphalerite, galenite, &c., the reaction is more sluggish. From an examination of the excess of sulphur monochloride in these different experiments it would seem that the original sulphur of the mineral is merely dissolved out, for upon evaporation it separates in large quantities.—*Journal of the American Chemical Society*, vol. xx., No 4.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 45).

THE foregoing tables and accompanying remarks, including several sentences preceding the tables, have been largely taken from the writer's paper entitled "A Plea for Greater Completeness in Chemical Rock Analysis," published in the *Journal of the American Chemical Society* (vol. xvi., pp, 90—93, 1894), also in the CHEMICAL NEWS (vol. lxix., p. 163, 1894).

Scope of the present Paper.

The literature relating to analysis of silicates is extensive, but scattered; and the scheme given by Fresenius in his "Qualitative Analysis" answers well for the ordinary separations, and is probably almost universally followed in all its essential features; but in no single article, to the writer's knowledge, is there to be found an exposition of the methods to be followed, or the precautions to be observed in the search for some of the

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

rarer constituents or those which, without being rare, have been of late years recognised as occurring persistently in small amounts. It is not the object of the writer to make this paper a treatise on mineral analysis; but it is believed that the experience gained by the chemists of this Survey during the sixteen years since the establishment of its first chemical laboratory in Denver may be useful to most chemists interested in mineral and especially rock analysis. Lengthy descriptions of details of manipulation will be avoided so far as possible, and in general only an outline will be presented of the methods followed or recommended, since in the main they are familiar to all or easily accessible; but stress will be laid on those points meriting particular attention, and now and then a brief discussion of alternative methods may be attempted.

In the earlier years of the existence of the Washington laboratory opportunity was afforded for the testing of novel methods and the devising of new ones, with most excellent results, as shown especially by the methods for separation of titanium, of lithium, and of boron, due to Prof. F. A. Gooch, to whose inventive skill chemists owe likewise the perforated filtering crucible and the tubulated platinum crucible arrangement for the estimation of water. Of late years the press of routine work has been such as to fully fill up the time of the much-reduced chemical force, and as a consequence it has been found impossible to subject to critical trial several separation methods of recent origin, some of which seem to be full of promise, or to follow out certain lines of investigation which have been suggested by the observations made in this laboratory, one, at least of which, seems to be of high importance. This, then, must be offered in explanation, if, in the following discussion, it may seem to some that any of the methods followed are too conservative or not sufficiently up to date. In general the discussion will be confined strictly to such separations as may be required in the analysis of an igneous, metamorphic, or sedimentary silicate rock of complex mineralogical composition, in which the majority of, and possibly all, the ingredients in the list given below may occur in weighable or readily discoverable quantities:—

SiO_2	TiO_2	ZrO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	FeO
NiO	CoO	CuO	MnO	CaO	SrO	BaO
MgO	K_2O	Na_2O	Li_2O	H_2O	CO_2	C†
SO_3	S*	N	Fl	Cl		

* Usually as pyrite, not infrequently as pyrrhotite.
† As graphite or coaly matter.

The special problems often arising in the analysis of rocks of extra-terrestrial origin—the more or less stony meteorites—will not be considered in this paper. An analysis of that kind should never be entrusted to the novice, but only to the chemist who has a knowledge of the composition and properties of the peculiar mineral constituents of those bodies, and a judgment fit to cope with the oftentimes difficult problems presented by them.

Thorium, cerium, and other rare earths are seldom encountered in quantities sufficient to warrant the expenditure of the time necessary for their isolation. A search for them qualitatively, even, is at present rarely justifiable unless there is microscopic or other evidence of the presence of minerals likely to contain them. Vanadium, tantalum, columbium, boron, and glucinum have never been certainly met with in the writer's experience, and yet they must be present in certain rocks, and doubtless traces have been overlooked at times. There is no reason to suppose that other elements may not be found by careful search, possibly all in the known category, and, indeed, Sandberger's researches have shown to what an extent this is true of a large number of those elements contributing to the filling of metalliferous veins. But those in the above list may usually be estimated with ease in weights of from one-half to 2 grms.

If the point be raised that many of the published analyses emanating from the Survey laboratories, even the earlier ones of the writer, are not in accord with the advocacy of completeness contained in the foregoing pages, it may be remarked that these ideas have been to a considerable degree evolved during a personal experience of sixteen years in this line of work, and that frequently the exigencies were such as to compel restriction in the examination. Where the latter has been the case subsequent developments have in some cases shown it to be bad policy in every respect. It is better, both for the geologist and the chemist, to turn out a limited amount of thorough work than a great deal of what may prove to be of more than doubtful utility in the end.

In this connection the question has often been put, "How long does it take to complete an analysis of this kind?" This will depend, of course, on the mineral complexity of the sample and on the personal factor of the individual worker. If there is a competent assistant to do the grinding, and specific gravity determinations are not required, it is quite possible after long experience for a quick worker to learn to so economise every moment of time in a working day of seven hours, with an abundance of platinum utensils and continuous use of air- and water-baths through the night, as to finish every three days, after the completion of the first analysis, barring accidents and delays, one of a series of rocks of generally similar character, each containing from eighteen to twenty quantitatively determinable constituents, excluding, for instance, fluorine, carbon as such, nitrogen, metals of the hydrogen sulphide group, and cobalt. On one occasion a series of fourteen rocks, of comparatively simple composition, was completed in one month, with the help of an assistant who made the phosphorus and ferrous iron determinations. But such an output of work is more than exceptional, and implies an unusual freedom from those occasional set-backs to which every chemist is exposed.

Part II.—*Discussion of Methods.*

Preparation of Sample.

Although foreign to the above heading, a few words relative to the sample itself may be here appropriately inserted by way of introduction. In the great majority of cases a few chips from a hand specimen will well represent the average of the mass, but with rocks in which a porphyritic structure is strongly developed the case is different. Here a large sample should be provided, gauged according to the size of the crystals, and the whole of this should be crushed and quartered down for the final sample. Unless this is done it is manifest that the analysis may represent anything but the true average composition of the rock.

Crushing.—Mechanical appliances for reducing samples to fine powder are much in use in technical laboratories, where they answer their purpose more or less admirably, and something similar is needed in those scientific laboratories where rock analysis is of daily occurrence and many samples must be reduced to fine powder in a short space of time. For accurate analyses the use of steel crushers and mortars is out of the question, because of the danger of contamination by particles of metal and the impossibility of cleansing the roughened surfaces after they have been in use a short time. Extraction of steel particles from the powder by aid of a magnet is quite inadmissible, since the rocks themselves, almost without exception, contain magnetic minerals. The method of rough crushing found to be most satisfactory in practice is to place each fragment as received on a hardened steel plate about 4½ c.m. thick and 10 c.m. square, on which is likewise placed a steel ring 2 c.m. high and of about 6 c.m. inner diameter, to prevent undue flying of fragments when broken by a hardened hammer. In this way a considerable sample can soon be sufficiently reduced for transfer to the agate grinding mortar with a minimum of metallic contamination.

Grinding.—Of the various grinding arrangements on

the market purporting to fulfil their purpose, few, if any, observed have met the conditions required by the work in hand. Either the mechanical arrangement is complicated or cumbersome, requiring more power or space than is usually at disposal, or causing too much noise, or thorough cleansing is difficult and troublesome, or there is likelihood of contamination from oil or grease, or lack of facility for the removal of all powder from the mortar. These last defects are especially prominent in those forms in which the mortar is fixed in its setting.

All rock samples have therefore been reduced to powder by hand, involving a great expenditure of time and labour. Ordinarily an extremely fine state of division is unnecessary, except in the case of those portions in which alkalies and ferrous iron are to be estimated, or where soluble constituents are to be removed by acids, &c., and in such cases the final grinding can be done at the balance table on a small portion slightly in excess of the quantity to be weighed off.

The process of sifting through fine cloth, the German "beuteln," is one not always to be commended, because of the time required, and, more especially, because of the certainty of contamination by cloth fibre, which in the ferrous-iron portion might affect the result. Still less should metal sieves be used.

Weight of Ground Sample.—The sample when ground should weigh not less than 10 grms, and preferably 20, in case it should be necessary to repeat or advisable to employ unusually large portions for certain determinations, notably carbonic acid. Rock analysis has in this respect an advantage over mineral analysis, since material is almost always available in ample quantity and any desired number of separate portions may be used, whereas with a mineral the analyst is frequently compelled to determine many or all constituents in a single, often very small, portion of the powder. This course often involves delay and the employment of more complicated methods of separation than are usually necessary in rock analysis.

Specific Gravity.

By Suspension in Water.—This determination, when required, is best made upon one or several fragments weighing up to 20 grms. They are held together by a fine platinum wire ready for suspension from the balance, and thus held are placed in a small beaker to soak overnight in distilled water under the exhausted receiver of an air-pump, side by side with a similar beaker of water. Boiling is of course a much less effective means of removing air than the air-pump, and the boiling water may exert an undesirable solvent and abrading effect. In the morning the wire is attached to the balance arm, the rock fragments remaining immersed in the water; a thermometer is placed in the companion beaker of water, now likewise in the balance case, and the weight is at once taken. Both vessels of water having precisely the same temperature, it is quite unnecessary to wait for the water to assume that of the balance should it not already possess it. The fragments are now lifted out, without touching the vessel, and carefully transferred to a tared crucible or dish; the wire is removed, and at once re-weighed, with the precaution that it dips just as far into the water now as when weighted. Hereby a special weighing of the wire out of water is avoided. The sample may now be dried on the water-bath, and then at 110° C. for some hours, to certainly expel all absorbed water, and weighed after prolonged cooling in the desiccator. It is better to ascertain the weight of the dry rock after soaking in water than before, in order to avoid the error due to possible breaking off of a few grains between the two weighings. Should the density of the rock in air-dry condition be required,* it may be left exposed to the air for a lengthy period after drying and before weighing; but the difference will only in exceptional cases affect the second decimal by more than a single unit. For instance, a rock of 2·79 specific gravity when dry will, if carrying the high percentage of 0·3 per cent hygroscopic moisture in the uncrushed state, have a density of 2·775; a rock of 3·00 specific gravity dry will have a density of 2·982 if 0·3 per cent of moisture is included.

Reasons for preferring Suspension to Pycnometer Methods.—This method of ascertaining the specific gravity of rocks is certainly more convenient than, and for compact rocks is believed to be decidedly preferable to, that of the pycnometer, in which the fragments must be reduced to small size with consequent formation of more or less powder, which is subject to slight loss in the various manipulations. To exclude this powder and employ only small fragments would introduce a possible source of error, since it is apt to consist largely of the most easily abraded minerals, and consequently not to have the average composition of the mass. By following the instructions given above, loss of material is absolutely avoided, a decided saving in time is effected, and considerable weights can be easily employed with consequent lower probable error in the results. To vesicular rocks, however, notably certain lavas, the above procedure is of course inapplicable, unless the datum is desired for certain considerations in which the relative density of large rock masses as they occur in Nature is sought, as for the comparison of building stones or the calculation of large known or assumed areas of particular rocks.

Pycnometer Methods.—If the pycnometer has to be used, as is generally the case when the density of any one of the mineral ingredients of a rock is desired after separation by one of the approved methods, it being then in a more or less finely divided state, the most accurate procedure is that adopted in this laboratory by Mr. L. G. Eakins a number of years ago. The pycnometer used is one with a capillary stopper, provided with a millimetre scale etched in the glass, the divisions being numbered both ways from the centre and calibrated by mercury, so that the value of each one in weights of water is known. The capacity of the flask filled with water to the zero division is then calculated for every half degree of temperature from 0° C. to 30° C., by making a series of careful weighings, in which, knowing the capacity of the stem, it is quite immaterial at what level the water stands provided it is within the limits of the scale. The exact temperature is secured by an accurate thermometer placed in a companion vessel of similar shape to the pycnometer and containing a like amount of water, both being left in the balance case till its temperature has been nearly or quite assumed, as shown by a second thermometer. The weighing must of course be made before the thread of water has sunk beneath the lowest division, which it will do after a time, even though at first filling the bore to the top of the stopper; and the corrected weight full of water to the zero mark is found by adding or subtracting the needed amount, as shown by the height of the thread on the scale.

For each pycnometer in use, and these are of different sizes, is prepared a table showing its weight, the value of each scale division in grms. of water, and the capacity of the flask at different temperatures, as indicated above. The preparation of such a series of flasks is time saved in the end, for the weighing of the flask full of water each time a density determination is made is rendered superfluous. All that is necessary is to look up in the table the weight corresponding to the temperature.

The density of the previously weighed substance in this case is now determined in much the same way, after the unstoppered pycnometer containing it, and nearly

* In view of the uncertainty as to what constitutes hygroscopic water, this course is perhaps more to be commended than the former, and seems imperative for certain zeolitic rocks. In such cases it is best to weigh the fragments before putting to soak, and afterward to collect on a Gooch crucible the grains which may have fallen off in the water. Should no crucible of this kind be available, a paper filter may unhesitatingly be used and incinerated with the powder, owing to the small amount of which the error due to loss o even all its water during ignition is quite negligible.

filled with water, has stood with its companion vessel of water under the air-pump the necessary length of time. The water needed to fill the flask is taken from its companion.

All who have used the pycnometer method for fine substances know the difficulty experienced in preventing a portion from being held at the surface, despite all attempts at making it sink. Hence it often happens that a very small portion runs out around the sides of the stopper on inserting it. If the flask rests in a small tared dish the grains thus forced out may be washed down into it and weighed after evaporation, in order to get the correct weight of that in the flask; or, after weighing, the contents of the flask may be emptied into a tared dish, and the water slowly evaporated off in order to get the weight of the mineral. Usually this way is less to be recommended than the other.

Penfield's Method for Mineral Fragments.—Penfield (*Am. Jour. Sci.*, 3rd Series, vol. l., p. 448, 1895) recommends the following modification of the suspension method as more convenient than that by the pycnometer in many cases for small fragments of minerals:—

After boiling in water, the substance is transferred with water to a small glass tube about 8 m.m. by 35 m.m., provided with a fine platinum wire for suspension. This is weighed full of water in another vessel of water, and again after the removal of the mineral, the weight of which is found after drying.

This method is, of course, more applicable to homogeneous minerals than to rock fragments, and will therefore be applied in rock analysis chiefly to the determination of the specific gravity of the mineral grains separated by heavy solutions or acids.

Heavy Solutions not available in case of Rocks.—Because of their roughness, porosity, and complex mineral composition, the density of rock fragments cannot be accurately determined by that of heavy solutions in which they may remain suspended.

Weights of Sample to be employed for Analysis.

With only occasional exceptions nearly all the constituents mentioned on page 56 can be estimated, if present, in 1 grm. of rock sample. This is a convenient weight to take for the main portion in which silica, alumina, &c., the alkaline earths, and magnesia are to be sought; but it should in general be a maximum, because if larger the precipitate of alumina, &c., is apt to be unwieldy. Its weight cannot often be much reduced with safety if satisfactory determinations of manganese, nickel, and strontium are to be expected. For the alkali portion one-half grm. is a very convenient weight. In general it may be made a rule not to use more than 2 grms. for any portion which has to be fused with an alkaline carbonate, as for sulphur, fluorine, chlorine. For carbon dioxide the weight may rise to 5 grms. or even more, if the amount of this constituent is very small, without expenditure of any more time than is required by 1 grm., and with correspondingly greater approach to correctness in the result.

(To be continued).

ELECTROLYTIC DETERMINATIONS.

By EDGAR F. SMITH and DANIEL L. WALLACE.

1. *Uranium.*

SOME years ago one of us found that it was possible to completely precipitate uranium (*Am. Chem. J.*, i. 329; Smith's "Electrochemical Analysis," p. 94) from an acetate solution by means of the electric current. The deposit consisted of the hydrated protosesquioxide of uranium, which was ignited and weighed as U_3O_8. Indeed, the procedure was adopted in the separation of uranium from the alkali metals when they were associated in certain rare minerals. It has frequently been used since that time by the author, and its reliability has been fully confirmed. However, Heidenreich (*Ber. d. Chem. Ges.* xxix., 1587) evidently experienced some difficulty in obtaining satisfactory results, for he remarks:—"Versuche, Uran aus seiner Acetatlösung quantitativ abzuscheiden führten zu keinem Ergebniss, selbst bei 50-stündiger Einwirkung des elektrischen Stromes." A method requiring fifty hours would scarcely be regarded as having value, even if the final results were really good. The following experiments, however, show that not only can satisfactory results be obtained, but they furthermore leave little doubt as to the time-factor, which is of prime importance in all determinations.

A solution of uranium acetate was prepared, which contained 0·1185 grm. of urano-uranic oxide (U_3O_8) in 10 c.c. of the liquid. To the latter volume were added 5/10ths c.c. of concentrated acetic acid, and the whole was then diluted to 40 c.c. with water, when it was electrolysed with a current N. D_{40}=0·18 A. V=3. The temperature of the liquid during the decomposition was 70° C. The uranium was completely precipitated in six hours. The filtrate or solution poured from the deposit showed no traces of uranium, when it was evaporated and the residue tested for that metal.

Results.

U_3O_8 present in grms.	U_3O_8 found in grms.
0·1185	0·1187
0·1185	0·1184
0·1185	0·1182

2. *Cadmium.*

Those interested in electrolysis will probably remember that the writers have at various times proposed methods and conditions not only for the electrolytic determination of this metal, but also for its separation from the more frequent associates. So often have we ourselves carried out these separations that we were inclined to believe other chemists would meet with like success. Such, however, seems not to have been the case, for in a very recent issue (*Journ. Amer. Chem. Soc.*, xix., 870) we felt called upon to publish very carefully outlined conditions for the complete deposition of cadmium from acetic and nitric acid solutions in order to again confirm our early statements. Heidenreich (*Ber. d. Chem. Ges.*, xxix., 1587) mentions that the separation of cadmium from solutions containing sodium phosphate and free phosphoric acid gave results which were "ebenfalls nicht quantitativ; die letzten Reste von Kadmium sind nicht zu entfernen, selbst wenn der Strom bis 1-Ampère verstärkt wird." We regret exceedingly that this chemist has met with so little success in his efforts to repeat our work, but, as in former instances of disagreement, we again present new experimental evidence showing that our original suggestions were undoubtedly correct.

To 10 c.c. of a cadmium sulphate solution, containing 0·1656 grm. of metallic cadmium, were added an excess of disodium hydrogen phosphate (1·0358 sp. gr.) and 1½ c.c. of phosphoric acid (1·347 sp. gr.). The liquid was then diluted to 100 c.c., heated to 50° C., and electrolysed with a current N. D_{100}=0·06 A. Volt=3. The precipitation was finished in seven hours. The metal deposits were bright and adherent. They did not show the slightest trace of sponginess. At the expiration of four hours the current was increased to N. D_{100}=0·35 A. Volt=7. The acid liquid was syphoned out without the interruption of the current. The pole separation, during the entire precipitation, equalled 1¼ inches. The cadmium was washed with hot water and then carefully dried. The filtrates were examined, but did not reveal a trace of unprecipitated metal. This is a direct contradiction of Heidenreich's statement that "die letzten Reste von Kadmium sind nicht zu entfernen."

Results.

Cadmium present in grms.	Cadmium found in grms.
0·1656	0·1654
0·1656	0·1658
0·1656	0·1657

—*Journal of the American Chemical Society*, xx., No. 4.

CORRESPONDENCE.

THE YEARLY INDEX TO "THE JOURNAL OF THE CHEMICAL SOCIETY."

To the Editor of the Chemical News.

Sir,—I fully sympathise with your correspondent "A Fellow of the Chemical Society" in his complaint of the long delay in the publication of the index to the *Journal of the Chemical Society* for 1897. I have never had the opportunity of knowing anything of the internal working of the Society, but, speaking as an outsider, it appears to be inexcusable that we should be well into July and the index for the previous year still remain unpublished. If the work were performed in the manner which common sense appears to indicate, the index would be ready for the printer immediately the December number of the journal was issued. I presume the members of the Council of the Chemical Society do not *use* the journal, or their self-interest would soon put a stop to the discreditable delay attending the publication of the index.—I am, &c.,

A Fellow of Thirty Years' Standing.

July 26th, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Physikalische Chemie,
Vol. xxv., No. 8.

Estimation of Dissociation Constants by Increase of Solubility.—Richard Lowenherz.—The author has limited himself to the proof of the fact that the dissociation constant can be calculated from experiments on solubility, and a few examples of the practical methods used for this calculation. He uses the bases aniline and *p*-toluidine of various concentrations, and the two acids cinnamic and *p*-nitrobenzoic. A number of small flasks, containing 250 c.c. of solution, are placed in a water-bath. The water used for solution must be distilled and freed from CO_2. In order to get the solutions quite saturated at the temperature of the experiment (25°), the solution is first raised to 35°, well shaken, and then allowed to remain at 25° for some hours. The liquid is filtered and titrated with 1/100 N baryta water, phenolphthalein being used as an indicator. The acids for the experiments are purified by being many times re-crystallised from water, and the bases by being boiled with lime and distilled.

Simultanous Application of the Law of Mass Action and the Phase Rule.—K. Kuriloff.—Unsuitable for abstraction.

The Variation with the Temperature of the number of Nuclei which are formed in Different Supercooled Liquids.—G. Tammann.—The author makes experiments on a large number of organic substances, and the chief conclusions he draws are:—(1) The number of points from which crystallisation can start in a supercooled liquid is excessively small in comparison with the number of molecules present. (2) The number of points increase with strong super-cooling until a maximum is reached, and then they decrease in a fairly symmetrical manner. (3). Foreign substances, whether soluble or insoluble, affect the number of nuclei. (4) The temperature of maximum nucleus formation is very slightly changed by the addition of a small quantity of the substance.

Investigations on the Influence of Mediums on the Reaction Velocity in Gaseous Systems.—Ernst Cohen.—Menschutkin and Carrara showed that the velocity with which a given reaction takes place is affected to a high degree by the character of the medium. The author extends this series of experiments to ascertain in how much the reaction velocity of gases varies when the same reaction takes place in various chemically indifferent mediums. He uses for his experiments AsH_3, obtained by the decomposition of pure As_2Zn_3 by dilute boiling H_2SO_4, in atmospheres of H, N, CO_2, &c. His experiments prove that the decomposition velocity of AsH_3 at 310° is not influenced by the presence of H or N, which result is in accordance with Nernl's theory.

Measurement of Electrical Conductivity in Dilute Solutions at a Temperature of about 100°.—R. Schalle.—The author shows, by means of experiment with a large number of organic and inorganic acids and their sodium salts, that the conditions of the electrodes exercise a great influence on the measurement of the conductivity of dilute solutions. The electrodes have previously to be boiled for some time with water, and in order to avoid the error as much as possible it is better to use small electrodes which are platinised, a little lead acetate having been added to the platinising solution. Vessels of Jena glass are used, as they practically resist the action of neutral salts and acids, when very dilute at 99°. The influence of the glass can be taken as constant, if measurements of it are taken with water. The following results are obtained:—(1) All electrolytes, when completely dissociated, increase their conductivity when the temperature is raised, the curve being linear. (2) The conductivity of acids which are not completely dissociated diminish with increase of temperature.

Combination and Substitution.—F. Wald.—Unsuitable for abstraction.

The Internal Friction of Electrical Solutions.—Hans Euler.—The author finds (1) that the internal friction of electrolytes depends on the friction of the ions and the undissociated portions, according to the equation $H = Sx + Ay + Ky$, where S = friction constant of the undissociated parts, x = its concentration; A and K = the friction constants of the anion and kathion respectively, y = their concentration. (2) There is a quantitative relation between the friction coefficient of the elementary ions and the migration velocity.

The Equilibrium Systems: Water, Ether, and Succinic Acid Nitrite.—F. A. H. Schreinemakers.—Unsuitable for abstraction.

Zeitschrift fur Analytische Chemie.
Vol. xxxvii., No. 3.

Estimation of Sugar in Sweet Wine and Polarimetric Investigations.—Arthur Bornträger.—The author refers to a former paper in which he describes the preparation of sweet wine simultaneously for polarimetric experiments and estimation of sugar. He repeats the treatment to prove the accuracy of the results, and also examines the effect of varying proportions of sugar and alcohol on the polarimetric observations.

Researches on Masut.—N. Kromer.—By the term "masut" is meant the residue left from the refining of petroleum oil. This substance is used in Russia for burning purposes. Specimens of this were examined, taken from various places, and all were found to have a black colour, a more or less viscous consistency, and an acid reaction. The portions taken for distillation were dried over calcium chloride. The distillation took place in an Engler's flask, and the boiling-points were noted; also the temperatures at which the oil burns spontaneously, which was very low in some of the specimens.

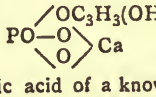
White Soda Lime.—Cl. Lageman.—The author has succeeded in preparing soda lime perfectly white, which he says can be prepared as cheaply as the ordinary grey substance.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xix.-xx., No. 7.

Action of Chloride of Aluminium on Anhydrous Chloral. — A. Mouneyrat. — 882 grms. of anhydrous chloral were placed in a dry flask of 1500 c.c. capacity, the flask was kept cool by means of iced water, and 167 grms. of finely-powdered, perfectly anhydrous, chloride of aluminium were gradually added, keeping the flask constantly agitated; after standing a few moments the mass becomes solid. The flask is then fitted with a vertical condenser, and heated on a water-bath; a regular stream of hydrochloric acid is given off; when this ceases, the still warm liquid is run into iced water slightly acidulated with HCl, and violently shaken; torrents of hydrochloric acid gas came off. A thick, heavy, brownish oil falls to the bottom, and after decanting and drying it is distilled fractionally; finally, at 120—121°, a small quantity of perchlorised ethylene ($CCl_2 = CCl_2$) is obtained, at 159—160° a considerable quantity of pentachlorethane, and above 160° a thick heavy oil with a strong choking odour.

Chloridation of Sulphide of Carbon in the presence of Chloride of Aluminium. — A. Mouneyrat. — In view of the powerful chloridising action of chloride of aluminium in the fatty series, the author wished to decide whether sulphide of carbon, chloridised in the presence of this powerful synthetic agent, would behave like iodine; he found that such was not the case, as the sulphide of carbon passes entirely to the state of tetrachloride before the sulphur can pass to the state of chloride, SCl_2.

Phosphoglycerate of Lime, and the Estimation of Neutral Phosphoglycerates.—MM. Adrian and Trillat. —The analysis of well-dried phosphoglycerate of lime, as obtained by the authors, gave:—Phosphoric acid, 32·93 per cent; lime 26 per cent, being very close to the formula—



If we add sulphuric acid of a known strength to a cold aqueous solution of a neutral phosphoglycerate, using heliantine as an indicator, the change appears the moment we have added half a molecule of acid for one molecule of the neutral salt: from this reaction a very rapid method of estimating neutral phosphoglycerates has been devised.

Contribution to the Study of the Reaction of Phosphoric Acid on Glycerin.—MM. Adrian and Trillat.—The observations made by the authors show that there is not yet a method known for obtaining phosphoglyceric acid in the pure state,—that the acid is decomposed by heat, and even by concentration *in vacuo*, re-forming phosphoric acid.

On Hydrocinnamide. — Marcel Delépine. — Hydrocinnamide, $C_{27}H_{24}N_2$, results from the union of cinnamic aldehyd, C_9H_8O, and ammonia, with elimination of water. Dehydrated hydrocinnamide dissolves easily in benzene, but separates out in impure yellow crystals, melting at 131°. Its heat of formation is −79·4 cal. (cryst.).

Synthesis of Terebic Acid.—E. E. Blaise.—Already inserted.

Camphoric Acid.—G. Blanc.

Constitution of Camphoric Acid.—G. Blanc.—These two papers are too long for useful abstraction, but the author claims to have proved that M. Bouveault's formula will explain all the facts yet known on the subject.

Two Coloured Reactions of Pyruvic Acid. — L. Simon. — If potash is first added to pyruvic acid, $CH_3—CO—COOH$, and then nitro-prussiate of soda, a beautiful intense violet-red colour is produced; by this means 1 part of pyruvic acid in 50,000 can be detected. If ammonia be added first, and then the nitro-prussiate of soda, a beautiful violet-blue colour appears after the lapse of a few minutes, but the limit of sensitivenes is only about 1 in 10,000.

A Coloured Reaction of Ordinary Aldehyd. — L. Simon.—Already inserted.

A New Coloured Reaction of Phenylhydrazin.— L. Simon.—Already inserted.

Thermic Study of Azelaic Acid.—G. Massol.—The quantity of heat given off by azelaic acid is less than that obtained with its normal homologues, even with those which have a fairly high molecular weight; it is +41·53 cal., suberic acid being 44·76 cal., and sebacic acid 43·09 cal.

Research on the presence of Hydrocyanic Acid in various Plants.—A. Hébert.—The author finds that hydrocyanic acid in plants does not occur in sufficiently large quantities to be protective. Certain Japanese plants which contain a comparatively large quantity are only seriously toxic in doses of 300 to 400 grms. Many others, containing a normal quantity, would require several kilos. to be ingested for any harm to be done.

MISCELLANEOUS.

West Ham Technical Institute.—The Council of the County Borough of West Ham have made the following appointments on the teaching staff of their new Technical Institute:—Lecturer in Physics and Mathematics: Mr. S. G. Starling, B.Sc., A.R.C.Sc. (Lond.), of the Battersea Polytechnic. Assistant in the Art Department: Mr. Mervyn Lawrence. Demonstrator in Physics: Mr. J. Tomkin, A.R.C.Sc., of the Royal College of Science. Demonstrator in Chemistry: Mr. F. H. Streatfeild, of Finsbury Technical College.

Institute of Chemistry of Great Britain and Ireland.—July Examinations, 1898.—Examiners: Professor Percy F. Frankland, F.R.S., F.I.C.; Otto Hehner, F.I.C.

Names of Candidates who Passed the Practical Examination for the Associateship (under Regulations in force prior to October 1st, 1893).—John Bristowe Pease Harrison, Yorkshire College, Leeds, and Registered Student under Thomas Fairley, F.I.C.; *Harold Nolan, M.B. (Lond.), Guy's Hospital and the British Institute of Preventive Medicine; *George Egerton Scott-Smith, Assistant to A. H. Allen, F.I.C.

Intermediate Examination (New Regulations).—Robert Duncombe Abell, University College, Bangor; William Arthur Cates, Finsbury Technical College; Walter Thomas Collis, Mason University College, Birmingham; Alexander Davidson, jun., William Smith Denham, and James Faill, Glasgow and West of Scotland Technical College.

Final Examination for the Associateship (New Regulations).—In Branch "A" (General Inorganic Chemistry): Leonard Myddelton Nash, King's College, London. In Branch "B" (Metallurgical Chemistry): *Frederic William Daw, Assoc. R.C.Sc. (Lond.), Royal College of Science, London. In Branch "D" (Organic Chemistry): Harry Thornton Calvert, B.Sc. (Vict.), Yorkshire College, Leeds; Robert Howson Pickard, B.Sc. (Lond.), Ph.D. (Munich), Mason University College, Birmingham. In Branch "E" (The Analysis of Food and Drugs, and of Water): Alexander Nash Crosskey, A.C.G.I., Central Technical College, London, and under J. Kear Colwell, F.I.C.; *Edward Russell, Charing Cross Hospital and St. Mary's Hospital. (Those marked with an asterisk for the Fellowship).

NOTES AND QUERIES.

Separation of Molybdenum.—Would some reader give a few references to reliable methods of *quantitatively* separating molybdenum from large amounts of iron. Processes dealing fully with the estimation of molybdenum in iron alloys would be especially valuable. References to English journals preferred —H. B.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2019.

ON THE YTTRIC EARTHS FROM THE MONAZITE SANDS.

By G. URBAIN.

I have already announced the results of my first researches on the fractionation of the ethylsulphates of the earths of the yttric group. My later researches on the same subject have only confirmed and completed the former. This method is especially suitable for separating these complex mixtures into groups of the bodies to which the already-described methods are best applicable. The inevitable presence of intermediate portions is principally due to the fact that the component parts of raw ytrria do not separate one from the other in an equally distinct manner. If it is an easy matter to obtain solutions containing erbium, perfectly free from holmium, it is extremely difficult to completely eliminate the erbium from the fractions rich in holmium. In the same manner if the earths of the terbia group are easily separated at first, the yttria present will be found in all the fractions.

The existence, previously pointed out, of a lower limit of fractionation of an atomic weight of about 97 has entirely to do with the difficulty experienced in separating yttrium from small quantities of the terbia earths. The greater part of these earths is generally precipitated by potassic sulphate, when we try to eliminate, by the aid of this reagent, the last traces of didymium kept in solution by the yttria earths, in such a manner that the yttria always remains contaminated with a certain quantity of the earths of the terbia group; this mixture, with an atomic weight of about 97, shows a remarkable persistence.

MM. Schutzenberger and Boudouard were the first to call the attention of the Academy to this limit of fractionation, but without having determined its exact nature.

I have admitted in a previous note that it contains principally yttrium, and I have since solved the problem in a complete manner, by isolating from this material yttria having an atomic weight of 89 and some earths of the terbia group of which the atomic weight reaches as high as 151·4, a figure which may still be below finality.

In the series of fractionations of the ethylsulphates which contain only yttrium, true erbium, and ytterbium, I was easily enabled to isolate yttrium with an atomic weight of about 89, by precipitations with ammonia. These fortunate results were due to the absence of the terbia earths. From this it appeared to be probable that by numerous crystallisations of the *heads* of the fractionations of the ethylsulphates (initial atomic weight 97) the terbias, if present in this material, would accumulate in the first crystals, in the same manner as was done by the didymium in the preceding fractionations.

Experiment fully confirmed these anticipations. After a sufficient number of crystallisations, the different fractions, transformed into oxides, gave tints varying from deep orange (*heads*) to those of a pale rose colour (*tails*).

These last retained a small amount of erbia, which was removed by crystallising the oxalates in nitric acid; the last mother-liquors from these fractionations were yttrium having an atomic weight of 89.

The coloured oxides belonging to the terbia group were characterised by the slight solubility of their formates. At any rate on being calcined in hydrogen they lost a scarcely sensible fraction of their weights.

They were transformed into a nitrate glass, and examined spectroscopically by reflection. I have only been able to detect two bands in the visible part of the spectrum.

Micrometer.		λ		
70	.. ..	0·000	Hardly seen.	Holmium.
122—130	.. ..	0·000	Intense.	Dysprosium.

These different characters suffice to show that this body is still complex in character; but the experiments prove that the yttria from the monazite sands contains principally yttrium with an atomic weight of 89, and that there does not exist an element whose atomic weight would be about 97 or 100.—*Comptes Rendus*, vol. cxxvii., No. 2, July 11, 1898.

ON THE HEAT OF FORMATION OF CARBIDE OF LITHIUM.

By M. GUNTZ.

To determine the heat of formation of this compound it suffices to measure the heat given off by the solution in water of a known weight of carbide of lithium; in this manner I have found that at about 17°—

$$C_2Li_2 \text{ sol.} + n H_2O \text{ liq.} = 2LiOH \text{ diss.} + C_2H_2$$
Disengaged gas .. .. + 37·10 cals.

This figure is the mean of three experiments which gave + 36·65, + 37·27, and + 37·25.

In order to do away with the correction due to the solubility of acetylene in the colorimetric liquid, the decomposition was effected in a glass apparatus plunged into the colorimeter: C_2H_2 was freely given off into the air. On each occasion the actual amount of the carbide used was verified by titration. In two of the experiments we took note of the free carbon, in the third we had pure carbide.

These data sufficed to calculate the heat of formation of carbide of lithium, knowing at the same time the heat of solution in water of lithium.

I thus found—

$$C_2 \text{ (diamond)} + Li_2 \text{ sol.} = C_2Li_2 \text{ sol.} \quad .. \quad +11{\cdot}3 \text{ cals.}$$

This is certainly a high number; it is much greater than the corresponding values found for CaC_2 and NaC_2; but it explains the easy formation of this compound under diverse circumstances.

To prepare Li_2C_2, I heat metallic lithium with carbon, but many precautions must be taken in order to ensure success.

In a glazed porcelain tube another tube of combustion glass was placed, and in this second tube was the iron boat containing the mixture of carbon and lithium (as a rule these two substances were present in equal proportions by weight). The porcelain tube was then firmly stoppered, the apparatus exhausted and then brought to a dull red heat for about half-an-hour.

If we make use of sugar charcoal for the carbon, even when strongly calcined, combination with incandescence takes place when operating on 2 or 3 grms. of lithium, on account of the formation of LiH; acetylene prepared by means of this compound always contains traces of hydrogen. Carbide of lithium is also produced, but without incandescence, when we use carbon which has been heated in the electric arc, or graphite. It is also formed by using diamond.

To prove this fact I heated, in vacuo, in a glass tube and an iron boat, a few fragments of cut diamonds; it is afterwards seen by examining the fragments of diamond under the microscope that the polish has disappeared by reason of the erosion which is characteristic of the reaction.

In the preparation of carbide of lithium it is necessary to use a double tube, because without this precaution the vapour of lithium attacks the porcelain tube, and in nearly every case causes a breakage; a vacuum is necessary, for at a red heat lithium absorbs all gases except argon. The tube must not be brought to a bright red heat,

because in vacuo the carbide of lithium dissociates too rapidly into carbon and lithium, in fact the dissociation even begins at a dull red heat.

By operating in the foregoing manner we obtain a greyish mass, sometimes coloured slightly yellow by iron; this is the carbide of lithium we wish to obtain. If it is heated for too long a time it will be contaminated by carbon. I have not been able to obtain this compound by the method which enabled M. Matignon to prepare pure carbide of sodium, on account of the readiness of melted lithium to attack glass, nor by M. Moissan's method as I had not sufficient electrical energy at my disposal.

By heating electrically 1 or 2 grms. of a mixture of $C_2+Li_2CO_3$, as described by M. Moissan, I always happened to entirely volatilise the whole of the carbonate of lithia, without obtaining a trace of carbide of lithium, which seems to indicate that a temperature high enough to volatilise Li_2CO_3 was still not sufficient to dissociate it into its elements and give free lithium, a condition necessary for obtaining the carbide.

Carbide of lithium possesses one very interesting property; when it is heated with melted chloride of lithium, or the fusible mixture LiCl+KCL, it decomposes, giving Li_2Cl and carbon; but at a high temperature Li_2Cl dissociates, giving LiCl+Li.

Lithium attacks the carbon set at liberty to reform the carbide; there is, therefore, an equilibrium formed at a high temperature, the reaction being reversible. This explains why we cannot make use of a carbon rod for the negative pole for the purpose of electrolysing LiCl, because at the temperature of electrolysis the lithium formed attacks the carbon and gives a carbide, which, by diffusing through the mass of the chloride, decomposes and gives carbon, which remaining in suspension in the liquid, impedes any useful formation of lithium.—*Comptes Rendus*, vol. cxxvi., No. 26, June 27, 1898.

ON THE LIMITS OF INFLAMMABILITY OF COMBUSTIBLE GASES.

By H. Le CHATELIER and O. BOUDOUARD.

The inflammability of gaseous mixtures is a most complex problem,—it must of necessity depend on most varying conditions, such as the heat of combustion, the speed of combination, &c. The work already done in this direction—unfortunately too little—has not formulated any precise relationships between the different phenomena which come into play. If we wish to sufficiently multiply the number of the experiments we must not confine ourselves to the combustible gases only, but we must include combustible vapours, which comprise a large number of compounds met with in organic chemistry.

To determine the limit of inflammability of a vapour—that is to say, the smallest quantity of this vapour which, when mixed with a definite quantity of air, is inflammable—we must not follow the same method as in the case of a gas. We have, in the case of very volatile liquids, such as ether, sulphide of carbon, and benzene, introduced successively known weights of these bodies into a flask of 2 litres capacity, previously full of air. A stirring apparatus, already in the flask, served to assist the evaporation, and also to render the mixture homogeneous.

The experiment was repeated until we obtained two separate weights, varying by at least 10 per cent, the weakest of which gave an uninflammable mixture and the strongest an inflammable one. The mean of these two numbers was taken as the limit of inflammability, which is thus within 5 per cent of the true figure.

In the case of slightly volatile bodies, such as the alcohols, essence of turpentine, or naphthalene, we should place the body in a 500 c.c. flask, kept at a constant temperature. A thermometer, to which a stirrer is attached, accelerates the saturation of the air. The temperature, corresponding to the limit of inflammability, has been determined to within 1 degree. To estimate the quantity of vapour existing in the mixture at this temperature, we passed a known volume of air (2 litres) through a small tube containing pumice-stone saturated with the liquid, and kept at the same temperature. The loss of weight gives the quantity of liquid which must be vapourised in order to furnish a volume of the mixture equal to 2 litres augmented by the volume of this vapour.

This method is, however, less exact than the preceding one, for two reasons:—On the one hand, the rapid variations in the vapour tension due to alterations of temperature; and on the other hand, by reason of the difficulty of perfectly saturating a given mass of air. The experimental errors by this second method may be at least twice as great as those by the first.

In the Table in which the results are collated, the letters at the heads of the columns have the following significance:—

t. Saturation temperature of the air.
p. Weight of vapour, per litre of the mixture, at a temperature of 15°.
v. Volume of vapour in 100 volumes of the mixture.
o. Volume of oxygen necessary for the complete combustion of the vapour.
q. Quantity of heat given off by the combustion of 1 molecular volume of the mixture,—that is to say, 23·5 litres at 15°.

The figures in modern type show the actual results of experiments; the others are calculated from these results by the known relations between the molecular weights and the heats of combustion.

Compounds experimented on.	*t*. Degrees.	*p*. Grms.	*v*.	*o*.	*q*.
Hydrogen	—	—	10	5	6·9
Carbonic oxide	—	—	16	8	11
Sulphide of carbon	—	0·063	1·94	5·9	4·9
Coal gas	—	—	8·1	9	10
Petroleum ether	—	0·045	—	—	13
Essence of petroleum	—	0·051	—	—	13
Petroleum oil	46·5	0·057	—	—	14·5
Methane	—	—	6	12	12·9
Pentane	—	0 034	1·1	9	9·5
Hexane	—	0·048	1·3	12·7	13·1
Heptane	—	0·047	1·1	12·3	12·9
Octane	—	0·049	1·0	12·6	13·1
Nonane	12	0·045	0·83	11·6	12·1
Acetylene	—	—	2 8	7	8·9
Amylene	—	0·046	1·6	11·9	12·8
Benzene	—	0 044	1·5	11	11·6
Toluene	—	0·049	1·3	11·4	11·8
Turpentine	30·5	0·042	0·73	10·2	10·9
Naphthalene	69	—	—	—	—
Acetone	—	0·073	2·9	11·6	12·7
Methyl alcohol	8	0·081	6	9	10·8
Ethyl do.	13·5	0·060	3·07	9·2	10·3
Propyl do.	25	0·065	2·55	11·5	12·5
Isopropyl do.	17	0·068	2·65	12	12·7
Isobutylic do.	27·5	0·053	1·68	10·1	10·8
Allylic do.	25	0·074	3·04	12·5	13·4
Amylic do.	38	0·045	1·19	9·0	9·5
Acetic acid	36	0·103	4·05	8·1	8·9
Ethylic oxide	—	0·060	1·9	11·7	12·5
Ethylic acetate	—	0·087	2·3	11·7	12·3
Nitrate of ethyl	—	0·145	3·8	—	12·2

Putting aside hydrogen and sulphide of carbon, of which the inflammabilities are very great, it will be noticed that for all the other bodies examined the heat of combustion of the mixture taken on 1 molecular volume is comprised between 9 cals. and 13 cals., and that that for most of them is between 12 cals. and 13 cals.; numbers which do not vary more than the possible errors of experiment. We are therefore warranted in stating, in a general manner, that the limit of inflammability of the

greater part of the carbon compounds corresponds to a heat of combustion of about 12·5 cals. The same table shows that the amount of oxygen consumed in the combination of these mixtures also varies very slightly from 11·5 of the total volume of the mixture.—*Comptes Rendus*, vol, cxxvi., No. 21.

LABORATORY NOTES.

By HORACE JERVIS.

Bottle Labels.

In a previous communication (Chem. News, lxxvii., 133) a solution of sealing wax is recommended for labelling bottles. Instead of lettering with a stiff brush, we find that a piece of glass tubing drawn out at one end is easier to use, and gives the letters a beaded appearance. When the solution is partially evaporated and somewhat thicker, a rubber tube joining the pen and the lips enables the sealing-wax to be forced out as required. In this way one can letter as quickly as with pen and ink.

The wax is not brittle when dry, and thus supplies a very durable as well as tasty means of lettering and numbering the backs of note-books. It may be used also for such purposes as waxing the $CaCl_2$ tubes of Geissler potash bulbs where heating tends to fracture the ground-glass joint. Such articles should then be dried in a water-oven.

Silicon in Steels.

Dudley's announcement that in steel analysis the dehydrated silica is re-dissolved, if allowed to stand after diluting, was reproduced in various journals (Chem. News, lxx., 186), without specifying that it referred particularly to Drown's process, in which the dehydration is affected with hot H_2SO_4. On this account the operators of various methods have scrupled to avail themselves of the convenience that a delay at such a point sometimes affords.

There are a number of methods in which the iron salts are evaporated to dryness, and the silica dehydrated by baking. Samples treated so might safely await the more convenient season in this baked state if it were not that, long after they have cooled, they sometimes fracture the bottom of the beaker. If, however, they be taken straight from the hot plate, and a stream of *hot* water be delivered round the inside of the beaker, this cracking is avoided, and, as we have satisfied ourselves experimentally, they may stand for days without error. This refers more particularly to a method in which the steel is dissolved in a mixture of sulphuric acid (125), nitric acid (208), and water (500).

Quantitative Estimation of Phosphorus in Phosphides.—Léon Franck.—During his researches on the compounds of aluminium with phosphorus, the author found considerable difficulty in estimating the phosphorus, owing to the fact that aluminium phosphides are very unstable in air. He has since devised a method which gives very accurate results. It depends on the oxidation of the evolved PH_3 by means of bromine, and the estimation of the phosphoric acid formed. A drawing is given of the apparatus. The phosphide is contained in a vessel connected with three tubes containing a saturated rolution of bromine in hydrochloric acid. Dilute sulphuric acid is dropped, from a dropping funnel, on to the phosphide, and the evolved gas passed into the bromine solution. The vessel containing the phosphide is connected with a Kipp's apparatus, evolving CO_2, by which the air is first driven out and afterwards the PH_3 into the bromine solution. The phosphoric acid in the three tubes is estimated in the usual way.—*Zeit. Anal. Chem.*, xxxvii., No. 3.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 58).

Water—Hygroscopic.

Importance of not Drying before Weighing.—The time-honoured custom of drying a powdered specimen before bottling and weighing has long seemed to the writer one that has no sound basis in reason. Its object is of course plain, namely, that of securing a uniform hygroscopic condition as a basis for convenient comparison of analytical results, since some rocks contain more hygroscopic moisture than others. Nothing, however, is more certain than that by the time the substance is weighed it has re-absorbed a certain amount of moisture, small, indeed, in most cases, but very appreciable in others; and further, with every opening of the tube moisture-laden air enters, and is enclosed with the remainder of the dry powder. It therefore may very well happen that a powder at first dry will, after several openings of the tube, especially at considerable intervals, be nearly as moist as when first enclosed.

It is preferable to weigh the air-dry powder, and to make a special determination of moisture at 100° or 110° C. If all the portions necessary for an analysis are weighed out one after another, or even at different times on the same day, the error due to difference of hygroscopicity in dry and moist weather, which for most of the separate portions is an entirely negligible quantity, is eliminated. Only in the main portion, in which silica and the majority of the bases are to be estimated, can it ever be an appreciable factor.

Temperature of Drying.—As to the temperature to be adopted for drying in order to determine so-called hygroscopic moisture, the practice has varied at different times and with different workers, ranging from 100° to 110° C. For the great majority of rock specimens it is quite immaterial which of these temperatures is adopted, since no greater loss is experienced at the higher than at the lower temperature, given a sufficient time for the latter. Since the drying is accomplished more rapidly at 110° than at 100°, it is the present practice in this laboratory to employ the higher temperature. Should the results show a very unusually high loss, the powder is re-heated at, say, 125°, in order to learn if the loss is progressive with increased temperature. In the affirmative case it may be well to repeat the drying at 100°, for a portion or the loss at 110° was probably due to combined water from a mineral or minerals in the rock; but in that case even the loss at 100° may sometimes very well include combined water, and a further drying over sulphuric acid alone may be desirable, or over dry sand.

Cautionary Hints.—In this latter connection it is proper to point out certain pitfalls in the path of the unwary, which, however, are far more apt to be encountered in the analysis of minerals, where their influence may be of far-reaching consequence.

A mineral which loses a great deal of water over sulphuric acid—2 or 3 per cent, for instance—may need an exposure of several days or even weeks for its complete extraction. If the weighings are made from day to day, the apparent limit may be reached long before all water really removable has been taken up by the acid. Whenever the crucible, after weighing, is replaced in the desiccator, it is no longer in a dry—but a more or less moist—atmosphere, and its contents, even when covered, sometimes absorb a part of this moisture, and retain it so persistently that the acid is unable to bring the powder beyond its previous state of dryness in the next twenty-four hours. In fact, it may be unable even to reach it

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

unless greater time is allowed. An experiment on 1 grm. of tyrolite, made and published some years ago, seems to illustrate this point in part :—

Hours exposed.	Loss. Grm.
18	0·0231
26	0·0083
23	0·0029
24	0·0012
23	0·0008
24	0·0001
25	0·0003
24	0·0002
24	0·0003
48	0·0006
24	0·0002
283	0·0380

The experiment might reasonably have been considered ended after the 158th hour, when a loss of but 0·1 m.grm. was shown during twenty-four hours; but nevertheless a nearly steady loss of 0·3 m.grm. per day took place for six days more, and might have been longer observed but for the interruption of the experiment.

Again, it is sometimes desirable to determine the water given off by hydrous minerals in an air-bath at temperatures far above 100° C. To ensure accuracy this experiment should not be made in crucibles or dishes which must be cooled in a desiccator. One instance will suffice :—A grm. of a mineral mixture containing about 17 per cent of water, of which about 3 per cent was driven off at 100° and 8 or 9 per cent at 280°, was, after several hours' heating, placed in a desiccator over sulphuric acid and weighed as soon as cold, then replaced and again weighed the next day. It had gained 1½ per cent of its original weight, although the desiccator was tightly closed and the crucible covered, showing apparently a drying power superior to that of the acid.

A specimen of tyrolite was found on one occasion to lose 10·34 per cent at 280° C., and on another occasion 14·33 per cent. In the latter case the drying and heating at progressive temperatures had continued during a period of 528 hours, the weighings being made usually from day to day; whereas in the former the duration of the experiment was much shorter, and the intervals between weighings were but a few hours each.

Procedure in Special Cases.—For experiments of this nature the powder should be heated in a weighed tube, through which a current of dry air can be passed, and allowed to cool therein, or else the water given off should be collected and directly weighed in suitable absorption-tubes,* even though the long time often required is an objection to this latter method, since the absorption-tube may gain weight, other than that of the water from the mineral, sufficient to introduce an appreciable error.

The recent important research of Friedel (*Bull. Soc. Min.*, vol. xix., pp. 14, 94, 1896; *Comptes Rendus*, cxxii., p. 1006, 1896) well shows what errors are possible in the determination of this easily removable water, since he found that certain zeolites which had been largely dehydrated but not heated to the point of rupture of the molecular net, could then absorb, instead of water, various dry gases in which they might be placed,—as carbon dioxide, ammonia, carbon disulphide, and others, even air in large quantities, and certain liquids. In the light of this observation, the cause of the great increase of 1½ per cent in weight of the partially dehydrated mineral mentioned above may very possibly be attributed to air from the desiccator instead of moisture, as was at the time supposed. At any rate, as Friedel says, the danger of accepting a loss in weight as an index of the amount of water lost is clearly shown, and thus that method of determining water is for many cases fully discredited. Just what method to adopt must be largely left to the judgment of the operator, who will often be guided by the mineral composition of the rock as revealed by the unaided eye or the microscope.

Friedel (*loc. cit.*) indicates a means for determining the true weight of water lost by minerals behaving like the zeolites, even without collecting the water lost, namely, by driving out of the dehydrated and weighed mineral, under proper precautions, any air it may have absorbed in the process of drying and cooling, and collecting and measuring this air and thus finding its weight, which, added to the apparent loss, gives the true contents in water.

Argument in favour of including Hygroscopic Water in Summation.—The question has been asked :—"If the so-called hygroscopic water is not always such, but not infrequently includes combined water, why is not its determination and separate entry in the analysis entirely unnecessary? Why make a distinction which, after all, may not be a true one?" The question involves the further consideration of the advisability of including in the analysis at all the loss at 100° or 110° C. Many petrographers desire to have all analyses referred to a moisture-free basis, in order that they shall be strictly comparable, and therefore would omit the "hygroscopic" water from the list of constituents. This would be eminently proper were it always possible to be sure that the loss at 100° truly represents mechanically held water. Since it very often represents more, and the determination as to whether or not it does in each case is not always possible, and would add to the time required for the analysis, it seems necessary to include this water. What errors may arise from its exclusion the following rather extreme case well illustrates :—Certain rocks of Wyoming in powder form lost from 1 to 2 per cent of moisture at 110°. That not even an appreciable fraction of this was truly hygroscopic the fact of the uncrushed rocks losing the same amount fully demonstrates; yet the rule followed by many chemists and petrographers would have involved the removal of all this water as a preliminary to beginning the analysis, and not only would a most important characteristic have passed unnoticed, but the analyst would have reported an incorrect analysis, inviting to false conclusions and possibly serious confusion.

Separate Entry of Hygroscopic and Combined Water.—To revert now to the primary question, it may be said that the estimation of the loss at 100° or 110° C., and its separate entry in the analysis, is advisable as not infrequently affording at once to the lithologist an indication of the mineral character of one or more of the rock constituents, thus perhaps confirming the microscopical evidence or suggesting further examination in that line. An unusually high loss at 100° would be regarded as probable evidence of the presence of zeolites or other minerals carrying loosely combined water. It has been objected that the true hygroscopic moisture varies with the degree of comminution of the sample and with the condition of the air at the time of weighing, and that it is therefore improper to incorporate it in the analysis; but this variation is ordinarily not at all great. Perhaps the time may come when it will be the rule to ascertain by additional heating at a higher temperature whether the water lost at 100° is to be regarded as purely hygroscopic. In such case it would be proper to omit it, and a distinct advance would undoubtedly be scored.

Is all true Hygroscopic Water expelled at 100°?—It has been tacitly assumed in the foregoing that true hygroscopic water can all be expelled at 100°, which perhaps is not to be accepted as universally true. Eminent authority holds that it is impossible, in the cases of certain foliaceous minerals, notably the micas, to thus entirely remove it, but that a part is only driven off at higher temperatures. If this is true a further uncertainty is introduced in its determination, which not only strengthens the argument

* Jannasch and Locke (*Zeitsch. für Anorg. Chemie*, vol. vi., p. 174, 1894) describe and depict a form of apparatus adapted for either method of ascertaining hygroscopic water.

in favour of entering all water in the tabulation, but also serves to emphasise the difficulties of the situation.

Water—Total or Combined.

Arguments against "Loss on Ignition" Method.—In a few cases the simple loss on ignition of a rock will give the total water with accuracy, but in the great majority there are so many possible sources of error that this old-time method can rarely be used with safety. Only when the rock is free from fluorine, chlorine, sulphur, carbon, carbon dioxide, and fixed oxidisable constituents, can the loss be accepted as the true index of the amount of water present, and it is rarely that a rock is met with fulfilling these conditions, especially as to the absence of ferrous iron. Blast ignition in presence of carbon dioxide alone of the above list may give a correct result, after separate estimation of the carbon dioxide, provided this emanates from carbonates of the earths and not from those of iron or manganese. The long-maintained and still upheld idea, that in presence of ferrous iron a sufficiently correct result is obtainable by adding to the observed loss an amount needed for oxidising all ferrous iron, is not justifiable. There can be no certainty that the oxidation has been complete, especially in the case of readily fusible rocks, and at the high temperature of the blast a partial *reduction* of higher oxides is not only possible but sometimes certain. The inability to insure complete oxidation by simple ignition is illustrated in the case of precipitated ferric hydroxide, which has been ignited together with its filter-paper. If the quantity was in any degree large it is sometimes decidedly magnetic, presumably from presence of magnetic oxide, which no amount of heating wholly oxidises, especially in the larger grains.

Brush and Penfield's Method.—Direct weighing of the water evolved is, then, imperative in most cases, and, if no other volatile constituents are present, the beautifully simple method first used by Prof. G. J. Brush and extended by Prof. S. L. Penfield (*Am. Jour. Sci.*, 3rd Series, vol. xlviii., p. 31, 1894; *Zeitsch. für Anorg. Chemie*, vii., p. 22, 1894), leaves nothing to be desired for accuracy. It consists simply in heating the powder in a narrow tube of hard glass, enlarged at the closed end and provided with one or two further enlargements in the middle to hold the water and prevent its running back and cracking the hot glass. A capillary glass stopper, fitted in with rubber tubing, prevents the loss of water by circulating air currents. The tube being held horizontally, the bulb is heated to any required degree, either in the blast alone or the simple combination of blast with charcoal backing used by Penfield, which gives the white heat requisite for complete expulsion of water in some cases. Moistened filter-paper or cloth wound about the cooler parts of the tube insures condensation of all water. The heated end being finally pulled off, the tube is weighed after cooling and external cleansing, and again after the water has been sucked out by aspiration. For most rocks, as they contain little water, central enlargements of the tube are hardly needed.

How this simple apparatus is made to afford entirely satisfactory results, even when carbonates are present, is fully set forth in the paper cited.

Few rocks, comparatively, are altogether free from other volatile constituents; hence for refined work the application of this apparatus in the simple manner above set forth is limited. It may, however, be used with the addition of a retainer for fluorine, sulphur, &c., in the shape of calcium, lead, or bismuth oxides, or even with sodium carbonate.

In whichever way used the water found is the total water, from which that found separately at 110° C. may be deducted if desired.

Gooch's Apparatus.—Of more elaborate apparatus designed to be used with fluxes the tubulated platinum crucible invented by Dr. Gooch (*Am. Chem. Jour.*, ii., p. 247, 1880) is capable of affording most excellent service, and it is the one by which far the larger number of water determinations in this laboratory have been made. Since its manner of use is probably not generally known, some directions may not be amiss. A detailed description of the apparatus itself would not be clear without a figure; but it may be said that the form now used differs from that figured in Gooch's paper and his subsequent slight modification of it, in that the tubes for connecting with both the drying and absorption vessels are constructed wholly of platinum instead of lead glass, the vertical one being bent horizontally at right angles for convenient attachment to the drying towers, and the side one also bent at right angles, but downward, so as to admit of insertion in the rubber stopper of a U-shaped calcium chloride tube. The length of the vertical tube, including its horizontal part from top of cap, is 13½ c.m.; that of the side tube is 12 c.m. The end of the latter is drawn in slightly, so as to enter the rubber stopper of the absorption tube without scraping it. With tubes of the lengths above given there is absolutely no danger of their ends becoming hot enough by conduction to scorch or soften the rubber stopper or other connection.

The extra first cost of the platinum extension to these tubes over the lead-glass ends of Gooch's original and modified forms need hardly enter as a factor in the question of employment of this apparatus. The glass ends often break, and only a rich lead glass—not easily obtainable—can be used, since it alone will not crack at the joint with the platinum after cooling. In its present form the whole apparatus weighs approximately 88 grms.

As an adjunct to its convenient use there is needed an ordinary upright iron ring-stand, with one small sliding ring, and above this a sliding ring-burner provided with entering ducts for gas and air-blast. Still above this is another small ring, across which there is an arrangement of stout platinum wire, forming at the centre of the ring a secure seat for the upturned flange of the crucible proper. Both rings and burner can be clamped firmly at any height.

The rock powder, having been placed in the cylindrical crucible, is there mixed with not more than 3 or 4 grms. of fully dehydrated sodium carbonate,* or more of lead chromate if carbon is to be likewise determined, the crucible is sunk in its seat in the upper ring, and the tubulated cap is fitted on and attached to the calcium chloride drying towers on the one side, and to a sulphuric acid bulb tube on the other. Powdered sodium tungstate—free from arsenic, which would soon ruin the crucible lips—is now poured into the flanged lip in which the cap rests, and a metal vessel of cold water having been raised up by the lower ring until the platinum crucible is sufficiently immersed, the blast-fed flame of the ring-burner, or that of an ordinary blast-lamp, if at hand, is turned on to melt the tungstate. As soon as this is fused the flame is removed, and the salt solidifies and makes an air-tight joint, the test of which is the permanence of the column of sulphuric acid in the bulb tubes caused by the contraction of the air in the platinum apparatus as it cools.

After drying by a current of air at 110° C. for a couple of hours, more or less (see below), the absorption tube is interposed between the sulphuric acid bulbs and the apparatus, being fitted to the latter by its stopper, which is at other times closed by a glass plug, and while a slow current of air continues to pass the gradual heating and subsequent fusion of the flux is brought about by the blast-fed sliding ring-burner. When fusion is complete, as shown in the case of sodium-carbonate flux by the decided slackening of the gas current through the safety bulbs attached to the drying tube, the flame is extinguished and a current of air is allowed to continue until the apparatus is cold.

This apparatus suffers from the drawback of being slightly permeable to combustion gases at high temperature. The defect can be overcome by causing the flame

* This has been heated for a length of time to near its fusing-point over a free flame or in an air-bath, to decompose the bicarbonate it usually contains, and then placed in a desiccator.

to play upon an outer ordinary platinum crucible, kept permanently filled with sodium-potassium carbonate. This protective crucible, however, is soon ruined for other purposes, being distorted by the alternate expansion and contraction of the carbonate.

It has been found that if the operation is carried out expeditiously, and the final full heat applied for but a few minutes, the error due to penetrating water gases is inappreciable. This hastening may be rendered safer by using rather finely-powdered calcium chloride in the central section of the U-shaped absorption tube to avoid large air channels. Through this, or any apparatus based on similar principles, the air current should always be forced, not drawn. A warm blast directed upon the exit tube near its entrance into the absorption tube greatly shortens the time required, and is to be recommended.

In this apparatus only the water expelled above 100° to 110° should as a rule be determined, and to effect drying of the mixed mineral powder and sodium carbonate, after luting the tubulated cap on the cylindrical crucible with sodium tungstate, the tube is sunk through a round hole in the cover into a small cylindrical air-bath, which can be heated from beneath by the same ring-burner which is subsequently to fuse the flux. A slow current of air is then forced through and the drying satisfactorily accomplished.

The reason why it is unsafe to attempt estimation of "hygroscopic" moisture in this apparatus is, that the luting of the two parts must be done by direct application of a flame to the tungstate, and considerable water vapour may enter the apparatus and be in part retained by the dried sodium carbonate.

Chatard's Apparatus.—The platinum apparatus devised by Dr. Chatard (*Am. Chem. Journ.*, xiii., p. 110, 1891; *Bull. U.S. Geol. Survey*, No. 78, p. 84, 1891) overcomes the permeability of the metal to gases, and affords sharp results, moreover permitting of determining by direct absorption not only the hygroscopic water, but that which may be driven off at any desired temperature. It is, however, more costly than the Gooch apparatus, and the supposed non-liability to injury by warping, because of the protective layer of borax and asbestos, can hardly be considered as proved.

Penfield's Second Method.—Simplest of all, and permitting by the use of auxiliary arrangements such as shown in Chatard's paper of determining the hygroscopic as well as any other fraction of the water, is the glass tube arrangement described on page 37 of Dr. Penfield's article cited on page 65.

All of these apparatus, except the first-mentioned glass tube, permit of the estimation of other constituents besides water in the same portion if necessary, and by the use of lead chromate or potassium chromate instead of sodium carbonate, graphite, or the carbon of organic matter, can be simultaneously determined with the water.

To one accustomed to its use, and with a drying and suspension attachment permanently set up, the Gooch apparatus, considering its limitations above set forth, offers perhaps the most handy and convenient means for the determination of water in rocks. Its high first cost, in comparison with the glass tube, is fully made up in time by its durability.

Jannasch's Methods.—That most zealous deviser of improved methods in mineral analysis, Prof. P. Jannasch, has published, in the *Zeitsch. fur Anorg. Chemie* and the *Ber. Deutsch. Chem. Gesell.*, several papers dealing with the problem of water determination in minerals besides the one already cited. Beginning with lead oxide as a flux, he subsequently experimented with lead chromate, borax, and boric acid, finding all of these to give accurate results in most cases when his directions are carefully followed, but unfortunately not capable (with the exception, perhaps, of lead chromate), like sodium carbonate, of general applicability, since with certain minerals one or the other fails to effect complete decomposition or to retain all volatile constituents. Especially for these reasons, also because the methods have not been tested in this laboratory and because Prof. Jannasch is still engaged in extending the boric-acid method, their use is not at present advocated for rock analysis. Moreover, the rock must be in such an impalpable powder for the boric-acid decomposition that a half to one hour has to be expended in the grinding of 1 grm. or less — a serious consideration for the busy chemist.

(To be continued).

THE DETERMINATION OF SMALL QUANTITIES OF ALCOHOL.*

By FRANCIS G. BENEDICT and R. S. NORRIS.

THE methods for the determination of alcohol ordinarily in use are for the most part physical. By means of the pycnometer, vaporimeter, and ebullioscope, we are able to determine with reasonable accuracy the amount of alcohol present in alcoholic beverages and solutions, which seldom contain under one per cent of ethyl alcohol. When, however, the exact estimation of smaller quantities is desired, these methods are unsatisfactory.

The numerous chemical methods for the determination of alcohol depend for the most part on the oxidising action of potassium bichromate, chromic acid, or potassium permanganate. Only a small portion of the research on the oxidising action of these compounds has been done with reference to their oxidation of alcohol. This is partly explained by the previous existence of the physical methods of analysis above referred to and by the fact that while many organic compounds are completely and readily oxidised to carbon dioxide and water, alcohol is oxidised with great difficulty, the oxidation ceasing usually with the formation of acetic acid. The iodoform reaction and the blue colouration produced with a sulphuric acid solution of molybdic acid, furnish tests of the greatest delicacy, and for the most part investigators have been satisfied with a qualitative demonstration of the presence of alcohol when occurring in such small quantities as to preclude the use of the ordinary quantitative methods.

Bodländer (*Pflüger's Archiv*, xxxii., 398), pursuing an investigation similar to that for which the methods here reported were devised, *i.e.*, the estimation of the small quantities of alcohol eliminated in the urine and breath of man, used a standard solution of chromic acid in concentrated sulphuric acid, and estimated the alcohol by determing the amount necessary to completely reduce a given volume of this solution. He states that the oxidation of alcohol is complete; *i.e.*, the products are carbon dioxide and water. Bourcart (*Chem. Centrbl.*, 1890, i., 547), Heidenhain (*Ztchr. Anal. Chem.*, 1893, xxxii., 360), Freyer (*Chem. Ztg.*, xix., 1184; *Ztschr. Anal. Chem.*, xxxvi., 328), and Kuriloff (*Ber. d. Chem. Ges.*, xxx., 741), find, on the other hand, that the oxidation with chromic acid or potassium bichromate ceases with the formation of acetic acid. Rose (*Chem. Centrbl.*, 1888, 308), used potassium permanganate as the oxidising agent, and states that the alcohol was completely oxidised to carbon dioxide and water by decinormal potassium permanganate in a solution that contained 40 per cent of sulphuric acid.

Bodländer's method was tried and found not to give entirely satisfactory results owing to the formation and escape of aldehyd, the amount formed varying with slight changes in the manipulation. On the addition of a dilute solution of alcohol to the concentrated sulphuric acid solution of chromic acid, the odour of aldehyd can be easily detected. Furthermore the end-point is rather difficult to determine.

Potassium permanganate, in the presence of strong sulphuric acid, was tried as an oxidising agent. It was

* From the *Journal of the American Chemical Society*, xx., No 4.

necessary to heat the solution in order to complete the oxidation, and under these conditions the potassium permanganate is decomposed in the absence of reducing agents. It is believed, however, where only approximate results are required, that the conditions can be determined under which the oxidation is complete, while the decomposition of the potassium permanganate, other than that produced by the alcohol, is very slight. The method used was to mix a definite volume of decinormal permanganate with 40 per cent of its volume of concentrated sulphuric acid, in a glass-stoppered flask. To this mixture the solution of alcohol was added from a burette, in small quantities at a time, and thoroughly mixed with it by shaking. The excess of permanganate was then determined by titration against a standard solution of ferrous ammonium sulphate. For certain purposes in the investigation it was necessary to determine the alcohol vapour contained in a current of air, and since it was found that the permanganate solution was reduced by simply passing the air of the room through it, this reagent could not be used.

As we were not successful in securing the accuracy desired with any of the methods tried, it became necessary to devise one which would give fairly close results for solutions containing as low as 0·01 per cent of ethyl alcohol.

The method adopted depends on the oxidation of the alcohol by an excess of chromic acid in a concentrated sulphuric acid solution, and the determination of the excess of chromic acid by titration against ferrous ammonium sulphate solution, the end-point being established by a few drops of standard permanganate solution. The reagents required for the determination are—

1. A solution of chromic acid in concentrated sulphuric acid.
2. A solution of ferrous ammonium sulphate.
3. An approximately decinormal solution of potassium permanganate.
4. A standard solution of alcohol in concentrated sulphuric acid.
5. Chemically pure, concentrated sulphuric acid.

The chromic acid solution is made by dissolving 2·2064 grms. of chemically pure potassium bichromate in just enough distilled water to effect complete solution, and then making up to 500 c.c. with concentrated sulphuric acid, care being taken not to let the temperature rise to over 100° C. This corresponds to a solution containing three grms. of chromic anhydride in one litre. The reagent preserved in a glass-stoppered bottle is fairly stable.

For the ferrous ammonium sulphate (Mohr's salt) solution 40 grms. of the pure salt are dissolved in water, and, after the addition of 30 c.c. of concentrated sulphuric acid, the solution made up to a litre. Made in this way the solution is very stable, showing but slight changes on comparatively long standing.

The potassium permanganate solution is made by dissolving three and three-tenths grms. of the crystallised salt in a litre of water.

The standard alcohol solution is practically a solution of ethyl sulphuric acid in concentrated sulphuric acid. About two grms. of 5 per cent alcohol (see below) are weighed into a 50 c.c. graduated flask and concentrated sulphuric acid added slowly, keeping the mixture cool to prevent any volatilisation of alcohol by immersion in cold water. After 5 c.c. of the acid have been added in this way the flask is filled to the 50 c.c. mark and the solution mixed by pouring back and forth into a beaker.

The alcohol used in preparing the standard was one of the better grades of commercial alcohol. Its strength was determined with the admirable pycnometer described by Dr. Squibb (*Journ. Amer. Chem. Soc.*, xix., 3). This pycnometer readily gives the specific gravity of alcohol to the fifth or sixth decimal place. Ostwald's pycnometer ("Hand-und Hilfsbuch zur Ausführung physiko-chemischer Messungen," W. Ostwald, p. 110), which has the advantage of being much cheaper, was also found to give quite satisfactory results.

An accurate table for determining the per cent of alcohol in solutions containing 40 per cent of absolute alcohol or over, from the specific gravity, is given by Dr. Squibb in his "Ephemeris" (*Ephemeris*, ii., 541). For solutions containing less than 40 per cent the table ("Bulletin No. 46, Division of Chemistry, U.S. Department of Agriculture," p. 65) used by the Association of Official Agricultural Chemists, is to be recommended.

A practical difficulty arises in weighing out small quantities of strong alcohol owing to its volatility. It is therefore recommended that an approximately 5 per cent solution be first made, from which small quantities can be correctly weighed without material loss. For preparing this solution the following method was found to be the most satisfactory:—A glass-stoppered Schuster dropping bottle, such as is ordinarily used to contain indicators, was weighed when dry and clean. After adding about the required quantity of alcohol its weight was again taken. The alcohol was poured into a previously tared flask, the last traces being removed by careful washing with distilled water. The solution was then made up to the desired weight, and the per cent of absolute alcohol in it calculated.

It is of the utmost importance that the concentrated sulphuric acid used in these experiments be free from organic or other reducing matter.

To find the value of each solution in terms of the other, the ferrous ammonium sulphate is first titrated against the potassium permanganate. A measured volume of the chromic acid solution, generally 10 or 20 c.c., is then poured into 100—200 c.c. of water, enough of the ferrous ammonium sulphate solution added to completely reduce it, and the excess of ferrous ammonium sulphate determined with the potassium permanganate. Twenty c.c. of a chromic acid solution of the above strength oxidises about 17 c.c. of the ferrous ammonium sulphate solution. Owing to the viscosity of the chromic acid solution it is necessary to adopt a definite method of delivery in order to obtain the same quantity each time. This result was secured by allowing the solution to run freely from an ordinary pipette made to deliver 10 c.c. Toward the end of the delivery the drops ceased quite suddenly to fall in quick succession, and followed each other only at intervals of several seconds. The first "slow" drop was taken and the pipette removed immediately. This method apparently gave equal volumes of liquid.

The amount of chromic acid required to oxidise a given weight ol alcohol was determined by means of the standard solution of alcohol in concentrated sulphuric acid. Ten c.c. of chromic acid solution were drawn off into a small flask, and a measured amount (about 3 c.c.) of the standard solution of alcohol added from a burette.* The mixture was heated with constant agitation over a free flame to 98° C.† (a thermometer being held in the solution) and kept at about this temperature for five minutes. Under these conditions no aldehyd was formed. After cooling the solution it was poured into 200 c.c. of water, ferrous ammonium sulphate added from a burette until the red colour of the chromic acid had entirely disappeared, and the excess of ferrous ammonium sulphate titrated back with the potassium permanganate.

The standard solution of alcohol used contained 237·6 m.grms. of alcohol in 100 c.c. In four titrations of this solution we obtained the following results. (See Table, next column).

Since a cubic centimetre of the alcohol solution contained 2·376 m.grms. of alcohol, 1 c.c. of the ferrous am-

* Considerable time is required for the sulphuric acid solution to run down the sides of the burette. The readings should not, therefore, be made until it is ascertained that the meniscus is stationary.

† According to Cross and Bevan (*Journ. Chem Soc.*, liii., 889), chromic acid in concentrated sulphuric acid solution gives off oxygen at 105° C. Numerous tests showed no decomposition of the chromic acid solution after five minutes' heating at 98° C.

	Alcohol solution. C.c.	Equivalent in ferrous ammonium sulphate solution. C.c.	Ferrous ammonium sulphate solution equivalent to 1 c.c. of alcohol solution. C.c.
I.	4·00	9·70	2·43
II.	4·95	12·00	2·42
III.	2·95	7·20	2·44
IV.	3·10	7·60	2·45
		Average..	2·43

monium sulphate solution would be equivalent to 0·978 m.grms. of alcohol. This factor was used in calculating the alcohol in the other solutions.

In order to test the accuracy of the determination, solutions of different strengths were made by the method used in preparing the standard solution.

The following results were obtained upon analysis:—

	Weight of alcohol. Calculated. M.grms.	Weight of alcohol. Found. M.grms.	Volume of solution. C.c.	Per cent of alcohol. Calculated. Per cent.	Per cent of alcohol. Found. Per cent.
I.	38·18	38·18	100	0·038	0·038
II.	30·63	30·05	50	0·071	0·070
III.	853·00	885·00	500	0·171	0·177
IV.	7·24	7·12	100	0·00724	0·00712
V.	11·01	11·23	50	0·02202	0·02246

An extremely dilute solution was made by diluting 12·34 m.grms. of alcohol to 250 c.c. The solution therefore contained 0·00494 per cent of alcohol. The result obtained by titration was 0·00508 per cent, an error of about one ten-thousandth of 1 per cent of alcohol.

In order to compare the accuracy of the method with that of Squibb's pycnometer for dilute solutions of alcohol, 31·44 grms. of 90·61 per cent alcohol was made up to 994·5 grms. with water, giving a 2·865 per cent solution. With Squibb's pycnometer the result was 2·95 per cent when calculated from a table in the "Ephemeris" (ii., 563), and 2·84 per cent when calculated from a more recent table (*Bulletin No.* 46, p. 65, Division of Chemistry, U.S. Department of Agriculture). By titration with the chromic acid the strength was determined to be $2\frac{8}{10}$ per cent.

As previously stated, one of the conditions to which the method must apply, was the determination of small quantities of alcohol in an air current.

Concentrated sulphuric acid, according to our experiments, removes alcohol from an air current even more completely than it does water. The apparatus with which this great affinity of sulphuric acid for alcohol was determined consisted of a system arranged as follows:—A current of air drawn by means of an ordinary Chapman filter-pump passed successively through a U-tube filled with cotton, a gas-washing cylinder containing concentrated sulphuric acid, a U-tube filled with soda-lime, a U-tube containing a known amount of alcohol, a cylinder similar to the first containing concentrated sulphuric acid, a 12-inch piece of combustion tubing containing a layer of copper oxide kept at a red heat by a four-tube burner, and a U-tube containing glass beads covered with about 10 c.c. of barium hydroxide solution, which in turn was connected by a rubber tube to the filter-pump. The tube with cotton was used to remove dust from the air. The sulphuric acid in the first cylinder removed the water, and the soda-lime the carbon dioxide. The air then passed over the alcohol and carried some of it into the sulphuric acid in the second cylinder. In case any of the alcohol was not absorbed by the sulphuric acid it would be burned by the hot copper oxide to form carbon dioxide, which would produce a precipitate in the barium hydroxide solution. Air was passed through the apparatus at the rate of 600 c.c. a minute.

(That it is possible to remove the alcohol quite completely from a current of air passing at a much more rapid rate than this, was subsequently demonstrated with a slightly modified apparatus. Owing to the fact that a rapid air current caused the combustion of the rubber stopper in the end of the short tube containing the copper oxide, by the hot air drawn against it, a tube 30 inches long was used and heated only at one end. The barium hydroxide U-tube in the apparatus above described also was not very satisfactory for rapid currents of air, and was therefore replaced by a gas-washing cylinder containing about 20 c.c. of barium hydroxide solution. A current of air containing alcohol vapour drawn through this apparatus at the rate of 2100 c.c. a minute, produced only a slight turbidity in the barium hydroxide solution in the course of fifteen minutes. When the cylinder containing sulphuric acid was removed from the system, however, a heavy precipitate was instantly formed).

(To be continued).

ON THE

PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.*

PART I.

By JAMES LOCKE.

THE problems set before the inorganic chemist by the periodic system, which have directly or indirectly guided almost all the inorganic investigations of the past thirty years, may be divided, roughly in the abstract but very sharply in the results obtained, into two classes. The one, of the fruitfulness of which no one can complain, deals with the superficial group-relations which exist between the members of the various families. Their solution leads to what may be called the development of group analogies. The problems of the second class, on the other hand, have either been entirely neglected, or their study has yielded only the most unsatisfactory results. These have had to do with the contractions of fact which the system, as formulated by Mendeleeff, involved, and to which the system should in course of time adapt itself. But all the more important inconsistencies which it presented in the year 1870 still remain, and are finally recognised as facts which, for the sake of a convenient principle, must not be forced into a conspicuous position. The behaviour of the elements of low atomic weight; the appearance of one and the same element in more than one degree of oxidation; the properties of the platinum metal; either receive no expression in the system, or they stand in direct contradiction to its laws. The difficulties involved, however, are confined chiefly to the compounds. The relations between the elements, *as elements*, are in almost every case clearly pointed out in the usual tables. This is true in regard to both the physical and chemical properties of the elements themselves. In this paper, therefore, only that part of Mendeleeff's law will be discussed which says that the *nature of the compounds of an element is also a function of its atomic weight.*

Of the 65 elements having places in the system, 9 of them, iron, cobalt, nickel, and the platinum metals, are put in a vertical row by themselves where they form the so-called 8th family, a family which may be said to fall outside the system proper. In this group many of the regularities which can be traced through other families are wanting.

The valency of the elements increases by one in each successive vertical row of the system, until the fourth is reached, after which each family yields two series of compounds, the one of increased, the other of decreased valency. In the potassium-nickel series, for instance, the various elements should enter into compounds with the valencies:

$K^{I.}$, $Ca^{II.}$, $Sc^{III.}$, $Ti^{IV.}$, $V^{V.}$, $Cr^{VI.}$, $Mn^{VII.}$, $(Fe, Co, Ni)^{VIII.}$ $Ni^{VIII.}$, $Cr^{III.}$, $Mn^{I.}$.

* From the *American Chemical Journal*, xx., No. 7.

So, since chromium falls within the 6th family, the greatest weight is laid upon the fact that chromic acid and its salts show such close analogy to sulphuric acid and the sulphates. The fact that potassium permanganate is isomorphous with the perchlorate, and like the latter only sparingly soluble in cold water, likewise assumes the utmost importance. If compounds of iron, cobalt, and nickel were known, in which these elements were octavalent, they, too, would possess the greatest theoretical value. But, with the exception of nickel carbonyl, a doubtful case of octavalency, these theoretically necessary compounds have never been obtained. Up to the present no one has succeeded in getting beyond the ferric acid of hexavalent iron.

That the decrease in valency, on the other hand, must stop before the 8th family is reached is obvious, for the 7th family is itself univalent, and a further decrease would prevent iron, cobalt, and nickel from forming any compounds at all. But this regularity ceases still further on—with chromium. No univalent manganese compounds have been obtained. Now, inasmuch as the iron, cobalt, and nickel compounds fail to conform with a regularity which can otherwise be traced throughout the entire system, they are assigned an entirely different rôle from that of other elements. They form transition stages, so to speak, from the manganous salts to the copper compounds of the next horizontal row. But this transition is not from the compounds of univalent manganese to those of univalent copper. Univalent manganese is unknown. It is from divalent manganese to divalent copper—to copper in a degree of oxidation which in no way corresponds to the position of this element in the system, and the salts of which have nothing more in common with the cuprous compounds, than has sulphuric acid with hydrogen sulphide; the same element can be obtained from both, and even then the road is by no means a smooth one, for directly before manganese stands chromium, and since divalent manganese has no place in the system, the chromous salts must be regarded as the true starting-point for the transition. But the transition from the unstable divalent and stable trivalent derivatives of chromium to those of ferrous and ferric iron is through a manganese in which the relative stability in the two degrees of oxidation is exactly the reverse.

I know I lay myself open here to the charge of expecting too much from the system. But why? Here is a great law of nature, the correctness of which no one can doubt. But in order to illustrate this law, an empirical arrangement of the elements is formed, and this arrangement we are all too apt to confuse with the law itself. The periodic system is satisfactory enough for the elements. Lothar Meyer's curves of the atomic volumes and melting-points prove this. For the compounds it is *unsatisfactory*. And in order to find out how the law does apply to compounds, we must sift out and discuss the discrepancies which the system shows in regard to them.

As with iron, cobalt, and nickel, so it is with all the other members of the 8th group. These metals, at the time of the promulgation of the periodic system, were assigned a position which, satisfactory though it was in illustration of their properties as elements, was in regard to their compounds absolutely abnormal; and no amount of investigation and speculation, with the periodic system as a basis, can clear up the contradictions which their position entails.

A second point upon which no light has been thrown lies in the behaviour of the so-called "typical elements." These, as Ostwald remarks, instead of being types of the families at the head of which they stand, have in the majority of cases properties directly at variance with those of the other members of their respective groups. In his "Principles of Chemistry" Mendeleeff says:—"The elements of the first two series have the least atomic weights, and in consequence of this very circumstance, although they bear the general properties of a group, still they show many peculiar and independent properties. These lightest elements are:—

H;
Li, Be, B, C, N, O, F;
Na, Mg, .., .., ...

As Mendeleeff left these elements, "typical," so they have remained, and the history of thirty years contains no mention of a successful attempt to unite them more closely than by that ill-fitting word to the groups to which they should show analogies.

Lithium is the lightest of all the elements having places in the system. It should, therefore, from the above, have the greatest number of independent properties of any of the typical elements. Or, one should at least expect to find metallic lithium and lithium compounds varying from the higher alkali metals and their derivatives in one and the same degree, since their departure from the rest of the group is conditioned by one and the same cause. The abnormal behaviour of the other typical elements should be along the same lines as in the case of lithium and its compounds. The essential properties of metallic lithium stand in strictest analogy to those of the other alkali metals. Metallic beryllium fits in accurately in the series formed by magnesium, zinc, cadmium, and mercury. Between boron and aluminium the analogy is less clear; but it appears again in full force in the properties of free carbon and silicon. The two elements show in their physical properties, allotropic modifications, and indifference to reagents, the strongest similarity. Fluorine and chlorine, in the elementary state, present the most striking analogies; and the gradations in character which the free halogens undergo with increasing atomic weight, from fluorine through to iodine, yield one of the most perfect chemical series imaginable.

Of the seven elements making up the first horizontal row, therefore, at least four possess, *in the elementary state*, properties closely akin to those of the subsequent elements in their respective families, and complete the series which the latter form.

Now, if the periodic system is true for compounds as well as for the elements themselves, then the compounds of analogous elements must be analogous—a simple deduction from the law which is not altered in its bearing, by the fact that the elements with which we happen to be dealing fall within the so-called typical class. If the low atomic weights, therefore, of the four elements, lithium, beryllium, carbon, and fluorine, are not of such influence as to prevent their ranking as they should, in their respective families, we must expect that their compounds will also show analogy to those of the other members of their groups. The compounds of lithium vary more or less from those of the other alkali metals, it is true; its phosphate and carbonate especially are less soluble; but, nevertheless, the lithium salts in general possess the characteristics of alkali derivatives, to an extent which would certainly prevent anyone from considering lithium as anything but an alkali metal. Carbon and silicon likewise bear close relationship in their compounds. The property of carbon which gives rise to organic radicals and existence of such a multitude of combinations between but a few elements, the ability of the carbon atoms to unite with one another, likewise appears in silicon. The silicon hydrides, the various chlorides, bromides and iodides, silicon-chloroform, and the complex oxygen compounds, such as silico-oxalic and mes-oxalic acids, illustrate fully the strong similarity between the influence of tetravalent carbon and that of silicon upon their compounds.

The law, and its expression by the periodic system, therefore, holds good in the case of lithium and carbon, and no fault can be found with the typical behaviour of the two elements. Now, if the effect of small atomic weight upon both lithium and carbon is too slight to cause in the nature of their compounds any great variation from that of their homologues, one has a perfect right

to assume that this separating influence will not be greater in an element which, in its atomic weight, lies between the two; but after a comparison, unprejudiced by the fact that an analogy between the compounds of beryllium and magnesium is required by their positions in the system, can a single trace of true resemblance be found between them, or between beryllium derivatives and those of any other element in the second vertical row? Magnesium hydroxide and beryllium hydroxide are both dibasic, it is true. But there the similarity ceases.

A strongly distinctive feature of all magnesium, zinc, and cadmium salts is seen in their behaviour toward ammonia and ammonium salts. They also have a pronounced tendency to form double salts with the compounds of other metals. Their oxides are insoluble in water, but soluble even in weak acids. Calcium, strontium, and barium, on the other hand, are characterised by their soluble, strongly alkaline hydroxides, by their difficultly soluble sulphates, and by the difficulty with which they enter into double salts. These are group characteristics, the presence of any one of which indicates the others. They give a tone to, and define the nature of, all the compounds of the two series. But to beryllium salts not one of them applies. Similar to magnesium though the metal be, its compounds show perfect indifference to ammonium salts; they form no double salts,* and the oxide is practically insoluble even in strong, hot acids; as little soluble, in fact, as alumina. This last fact, together with the ready solubility of the sulphate and of the fluoride, and the insolubility of the sulphide, &c., prevent any comparison of the beryllium compounds with those of the alkaline earths.

With fluorine, the nature of the compounds of which it will be unnecessary to discuss in full, the case is similar, although its atomic weight is nearly three times as great as that of lithium. The properties of the free element show it to be a pronounced halogen, with characteristics which one would expect to find in a halogen of lower atomic weight than chlorine. But its compounds are not only widely different from those of chlorine, but they often vary in a direction contrary to that of the gradations observed in the rest of the series. Fluorine, it is true, forms in common with the other halogens an acid of the type HR. But in distinction from hydrochloric, hydrobromic, and hydriodic acid, hydrofluoric acid has a remarkably low molecular conductivity; and its salts, in the majority of cases, have properties which are directly the opposite of those of the chlorides, bromides, and iodides. The most pronounced chemical characteristic of the halogen acids certainly lies in the solubility of their salts with heavy metals, and the insolubility of the silver, cuprous, and mercurous compounds. The *fluorides* of silver and mercury, on the other hand, are readily soluble: those of calcium, strontium, barium, magnesium, manganese, iron, cobalt, nickel, chromium, cadmium, copper, bismuth, lead, and others are either sparingly soluble or dissolve only in an excess of hydrofluoric acid. In the readiness with which fluorine enters into metallofluoric acids is seen another great distinction from the other halogens. In this, as in many of its other properties, it approaches very closely to cyanogen. Hydrofluoric and hydrocyanic acids and their salts have, in fact, little more in common with hydrochloric, hydrobromic, hydriodic acids, and the halogenides, than the fact that they are monobasic or derivatives of monobasic acids.

We have, therefore, in lithium, beryllium, carbon, and fluorine, four typical elements which in the free state, *as elements*, stand in close relationship to the other elements of their respective groups. In two of them, lithium and carbon, the influence of their low atomic weights is not such as to deprive their compounds of the chemical nature which characterises the derivatives of their analogues. The others, although one of them lies *between* lithium and carbon, and the other has an atomic weight almost large enough to take it out of the typical class, fail to show analogy to their homologues; that is, to satisfy the requirements of the system, as soon as they pass from the free state into combination.

These are contradictions which even the mysterious influence of a low atomic weight will not explain. They were known in 1870, and they stand to-day. With the development of organic chemistry, and the increase in the number of bodies known, which could not be explained by the laws of valency alone, stereochemistry appeared. Molecular compounds have been the subject of numerous theories, of which one at least, that of Werner, promises to bear fruit; but the inconsistencies shown, in reference to the other elements, by those of low atomic weight, the exceptions to a law more far-reaching than that of valency itself, have remained untouched, simply in recognition of the fact that it was hopeless to look for any explanation for them which could be reconciled to the system. And why? Because the inorganic chemist, in standing upon the periodic system, has been unable to dissociate in his mind the chemical compound from the elements of which its formula contains the symbols.

Of the work done in the development of group analogies little need be said. This has been the only successful field of investigation which the formulation of the system opened. But it may be well to point out briefly certain inconsistencies which are involved in the development of these analogies between neighbouring metals in the horizontal rows.

(To be continued).

* Certain double fluorides must be noted as exceptions to this statement. The double sulphates, phosphates, &c., known, may be disregarded, as they can be represented by simple constitutional formulæ, and this formation is of less significance than that of double halogenides, and the like. Both calcium and strontium yield double sulphates.

CORRESPONDENCE.

METARGON.

To the Editor of the Chemical News.

Sir,—Metargon is said to be an elementary substance having the primary characteristic of being a gas obtained by the volatilisation of a "white solid" (amounting to about one per cent), which separates during the liquefaction of argon, as stated by Prof. Ramsay and Mr. Travers in their Royal Society papers on the "Companions of Argon:"—"The argon separated as a liquid, but at the same time a considerable quantity of solid was observed to separate partially round the sides of the tube, and partially below the surface of the liquid." Further, "inasmuch as the gas differs very markedly from argon in its spectrum and in its behaviour at low temperatures, it must be regarded as a distinct elementary substance, and we therefore propose for it the name 'Metargon.' It would appear to hold the position towards argon that nickel does to cobalt, having approximately the same atomic weight for different proportions."

Now a year ago Lord Rayleigh was kind enough to allow me the use of a sample of pure argon for the purposes of liquefaction. The gas, amounting to 250 c.c., was enclosed in a sealed bulb, to which was attached a narrow quill tube for easy condensation in liquid air. I have repeatedly liquefied this sample, and have always obtained a perfectly clear fluid argon free from turbidity or opalescence. In previous papers I have shown that very small fractions of a per cent of impurity of a gaseous substance separating as a solid, the chief constituent being a liquid, under the experimental conditions, can be detected in this way. Thus the 0·04 per cent of carbonic acid in dry air gives an opalescent liquid air when similarly treated, and the same thing occurs with oxygen containing less than 0·1 per cent of chlorine. It would indeed be strange if anything like 1 per cent of a gas giving a white "solid at the

temperature of liquid air" could, under similar circumstances, escape detection, if present, in the Lord Rayleigh sample of argon. The question is, what has become of the metargon of Prof. Ramsay and Mr. Travers?—I am, &c.,

JAMES DEWAR.

Royal Institution,
August 2, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 21, May 23, 1898.

Further Researches on the Reactions Developed between Pyrogallol and Oxygen in the presence of Alkalis.—M. Berthelot.—The author finds that the oxidation varies considerably, according to the alkali present, either potash, soda, baryta, or ammonia. The observations and estimations made show that purpurogallol is generally formed. At the same time there is evidence that the pyrogallic molecule is destroyed by an oxidation which breaks up the fundamental cyclic system. This destruction may be imagined to take place in the following manner:—Of the three molecules of acetylene, which by their junction have helped to form a molecule of benzene—that is to say, a relatively saturated polymer—two are broken up and changed into carbonic acid and water, while the residue of the third remains united with three other molecules of the original pyrogallol in such a manner as to constitute a new and more complicated cyclic system of the triphenylethane order.

Phosphorescent Mixtures formed by Sulphide of Strontium.—J. R. Mourelo.—Various experiments are described with mixtures of sulphide of barium with sulphide of strontium, sulphide of strontium with sulphide of calcium, and sulphide of calcium with sulphide of barium. The results obtained have enabled the author to establish certain practical laws, which are of some interest:—To produce phosphorescence there must be at least 2½ per cent of either of the active bodies present; after this, the degree of phosphorescence increases with the proportion of the active body. In every case the exposure to light should be longer in the case of a mixture. Chloride of sodium or sub-nitrate of bismuth, added before heating, will always increase the phosphorescent power. As for the colour of the phosphorescence, that varies with the proportion of the different active bodies present in the mixture, but as a rule it is green that predominates.

Limits of Inflammability of Combustible Gases.—H. Le Chatelier and O. Boudouard.—(See p. 62).

The Spectral Analysis of some Non-conducting Minerals by their Melted Salts, and Reactions of the Elements.—A. de Gramont.—This article has already been inserted in full.

Synthesis of Safranine.—G. F. Joubert.—This paper is to a great extent the continuation of a discussion with M. Nietzki as to the correctness of the *asymmetric* formula of safranine; but it is shown that an estimation of the nitrogen and the chlorine gives the following results:—

	N per cent.	Cl per cent.
Calculated for $C_{20}H_{16}N_7O_6Cl$ ..	20·18	7·31
Found	19·84	8·02

Action of Chloride of Aluminium and of Chlorine in the presence of Chloride of Aluminium on Anhydrous Chloral.—A. Mouneyrat.—500 c.c. of anhydrous chloral were poured into a flask of 1000 c.c. capacity, fitted with a vertical condenser; then 250 grms. of perfectly anhydrous and finely ground chloride of aluminium were added a little at a time. The mass, then quite solid, was heated up to 75—80°, then, when the material was quite fluid, a current of dry chlorine was injected. This gas is entirely absorbed, and an abundant disengagement of hydrochloric acid gas ensues. After the lapse of some time, the interior surface of the flask, as well as the tube leading in the chlorine, become coated with magnificent white crystals having a very pronounced smell of camphor. When the chlorine is no longer absorbed, the then solid mass is put into dilute hydrochloric acid—a little at a time. Torrents of hydrochloric acid gas are then given off, as well as a small quantity of $COCl_2$, while a white powder, smelling slightly of camphor, rises to the surface. This body, which is purified by sublimation, melts at 187—188° in a capillary tube. Analysis gives it the formula C_3Cl_6.

Estimation of Phosphoric Acid in Superphosphates.—Leo Vignon.—The author points out that the method of estimation by difference is more to be trusted than that by the direct method. It is easy, he says, to understand why the ammonio-magnesic phosphate, by reason of its mass, has a greater tendency to deposit integrally in a mixture of water and citrate than in citrate alone, which might be poor in phosphoric acid.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxx., January 10, 1898.

Remarks on the Memoir by M. Hermann on the subject of the Number of the Isomeric Paraffin Carbides.—S. M. Losanitsch.—The author discusses the convenience of M. Hermann's method for calculating the number of isomeric saturated fatty carbides in C_n.

New total Synthesis of Glycerin and Dioxyacetone.—O. Piloty.—Dioxyacetone is easily obtained by adding 15 grms. of bromine to a solution of 10 grms. of its oxime in 100 c.c. of water. N_2O is given off, and the temperature rises to 40°. It is then neutralised with $PbCO_3$ and Ag_2O, and the filtrate evaporated at 30° *in vacuo*, taken up with absolute alcohol, and precipitated with ether. The syrupy precipitate is treated in the same manner, and at length a viscous product is obtained which solidifies over H_2SO_4; it is dioxyacetone. The return is 95 per cent of theory. It crystallises from boiling water in prismatic plates, fuses at 70—75°, is soluble in H_2O and organic solvents, except ether and ligroin. Dioxyacetone, $CH_2OH.CO.CH_2OH$, easily forms polymers, of which one is crystalline and melts at 155°, while the other is amorphous. The bisulphite compound, $C_3H_7O_5SNa$, crystallises in dilute alcohol in white needles.

Preparation of the Acetals.—E. Fischer and G. Giebe.—Many aldehyds can be transformed into the corresponding acetals by treating them with a dilute alcoholic solution of hydrochloric acid gas. Ordinary acetal was prepared by mixing 20 grms. of aldehyd with 80 grms. of alcohol containing 1 per cent of hydrochloric acid gas. It was left for eighteen hours in the cold; 100 c.c. of water containing sufficient K_2CO_3 to neutralise the HCl was added, and the product extracted with ether. The return was 60 per cent; with œnanthol, the return was 70 per cent. It boils at 205°. Dimethylformal can be obtained by treating formic aldehyd by 1·5 times its volume of alcohol containing 2 per cent of HCl, and 1·5 parts of $CaCl_2$. It is heated for fifteen hours and distilled. The acetal from glycolic aldehyd is prepared in a similar manner. The preparation of several other acetals is described. The process does not appear to be easily applied to the oxyaldehyds.

Tetramethyluric Acid.—E. Fischer.—This acid is prepared by the direct methylation of uric acid; it melts at 228° and has a bitter taste. One part of the acid dissolves in three parts of boiling water, twenty-seven parts of boiling alcohol, or thirty-nine parts of cold water. When heated with 1 per cent $POCl_3$ at 160°, it is transformed into chlorocafein. A 1 per cent solution of tetra-

methyluric acid, saturated with Cl, gives allocafein fusible at 206°. It is slightly soluble in water, and easily so in sulphuric acid and the alkalis. Boiling baryta-water decomposes it, giving mesoxalic acid. The oxidation of tetramethyluric acid is shown by the equation $C_9H_{12}N_4O_3+O+H_2O=C_8H_9N_3O_5+CH_3.NH_2$.

The Optical Properties of Tannin.—P. Walden.—Tannin is strongly dextrogyre, but the formula generally ascribed to it does not contain any asymmetric carbon. If we admit that tannin is not a definite chemical compound, but a mixture, then this anomaly disappears. In fact, the author has succeeded in separating several portions having entirely different rotatory powers, and he is of the opinion that tannin owes its activity to a foreign matter which is always present in variable, though small, quantities.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2020.

LABORATORY NOTES.

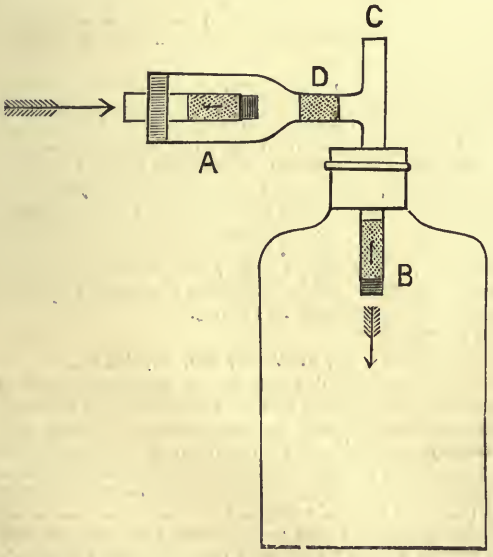
By HORACE JERVIS.

A Simple Pump.

The accompanying figure represents an apparatus which has been used at itinerant lectures to provide a stream of water, or air, or to serve as an air-pump.

It is necessary to perforate the rubber stopper so as to receive an additional tube, which should reach nearly to the bottom of the bottle. The piece of stout soft rubber tubing, B, is made into a Bunsen valve with a sharp razor. A similar valve is fitted into a glass tube, as at A. The other necessary part of the outfit is a cycle tyre inflater, which is attached to C, the open end of the T-tube.

On forcing down the piston of the inflater the air passes through the slit B into the bottle, and is prevented from passing through A, because the compressed air can act only on the outer circumference of the rubber tubing, and so more and more tightly closes the slit. On raising the piston the air is drawn through A, but, for the reason just stated, cannot pass through B again into the inflater.



The alternate motion of the piston then speedily accumulates air, under pressure, in the bottle, and it thus supplies—through the additional tube not shown—a stream of air, or, if water has been placed in the bottle, a stream of water. The arrangement admirably serves to illustrate the transmission of vibrations along a water column (Chichester Bell's experiment), or other phenomena of surface tension which may be illustrated by a thin stream of liquid.

If A (from the joint D) and B are changed about, then an upward action of the piston partially exhausts the bottle, and the downward motion drives the air through the valve B. If then the bottom of the bottle be cut off, the edges smoothed and fitted to a piece of ground glass, we have an efficient lecture-room air-pump.

It is hardly necessary to explain that a common form of tyre inflater is merely a rubber-tipped rod working in a brass tube, and so could be easily made. But they can be borrowed anywhere now-a-days.

ON THE ESTIMATION OF ARSENIC IN ANTIMONY AND IN OTHER METALS.

By O. DUCRU.

I. Metallic commercial antimony described as "purified" contains, as a rule, small quantities of iron, lead, copper, and sulphur, besides variable proportions of arsenic: the estimation of this latter body, which is particularly important with regard to certain of its applications, presents, as is well known, serious difficulties.

The method usually followed consists in dissolving the metal in an aqua regia containing an excess of hydrochloric acid, and in separating the sulphides insoluble in the alkaline sulphides: the sulphides of antimony and arsenic are in their turn oxidised, and the arsenic is precipitated in the form of ammonio-magnesic arseniate. Rivot, who described this method in some detail, previously isolated the sulphide of arsenic by treating with moderately dilute hydrochloric acid; he gives it as his opinion that this is sufficient for the estimation of the arsenic.

Independently of causes of error inherent in the use of the arseniate (solubility, carrying down of salts, &c.), this method leads to another which may be of importance:—On account of the volatility of chloride of arsenic, it is difficult to avoid losses, either during the solution of the metal or during the attack of the sulphides. It is easy to convince oneself of this, by carrying the vapours into an appropriate apparatus. There is also another thing: the proportions of arsenic found by different analysts, in the same sample of antimony, generally show considerable differences, and these are always below the truth.

II. This estimation can be made in a very simple and precise manner, by applying to an antimony a method described as the *distillation* or *ferric chloride* method, which is employed in the laboratories of certain works for the estimation of arsenic in metallic copper. (This method is due to Dr. John Clark, *Chem. Industry*, May 1887, p. 352). *The method of working is as follows:*—The sample for assay, about 5 grms., coarsely powdered, is placed in a tubulated retort, or a flask for fractional distillation, with 100 c.c. of ferric chloride prepared as follows, and 200 c.c. of pure hydrochloric acid of the ordinary strength (D = 1·17). The retort is united to a condenser* terminated by a tube plunging into a graduated flask containing 50 c.c. of water.

We then distil; the antimony is rapidly dissolved, and, each time that 100 c.c. have passed over, we add 100 c.c. of hydrochloric acid by means of a funnel placed in the top of the retort.

When 300 c.c. have been collected in this manner, all the arsenic will generally be found in the distillate; this is the case for proportions of arsenic reaching up to 10 per cent, a higher figure than is met with in practice.†

It is well known that under these conditions the distillate contains a little antimony; this is separated by a second distillation.‡

The receiving vessel is washed with hydrochloric acid,

* The use of condensers with large tubes is particularly convenient; the neck of the retort is drawn out and slightly curved.

† That all the arsenic has passed over in the distillate can be verified by passing a current of sulphuretted hydrogen through the hydrochloric solution *diluted with its own volume of water*; if there is no precipitate *after several minutes* all the arsenic has passed over.

‡ I shall eventually show how this second distillation can be avoided.

which is then added to the collected liquid; we thus get a total volume of about 400 c.c., which is distilled until 300 c.c. has passed over. All the arsenic will be found in this portion; this can again be verified by testing the liquid in the retort, diluted with its own volume of water, with a current of sulphuretted hydrogen. To arrest the first traces of hydrochloric acid passing over, it is advisable to put about 100 c.c. of water in the receiver.

This second distillation can be considerably shortened, by previously adding to the solution 50 to 100 c.c. of concentrated sulphuric acid; it will then generally be sufficient to distil 150 c.c.; it can be proved, as above, that all the arsenic has gone over. It is as well, in this case, to facilitate the distillation by keeping a small current of air passing through the boiling liquid.

The hydrochloric solution thus obtained is diluted with water and precipitated with hydrosulphuric acid. The precipitate of sulphide of arsenic is washed in the ordinary manner, and weighed on a filter or in a tared crucible.

III. *Preparation of the Solution of Ferric Chloride.*—We use a solution containing about 150 grms. of iron per litre, obtained by attacking 800 grms. of French nails by a mixture of 2 litres of pure hydrochloric acid and 2 litres of water: when the attack is ended, the liquid is saturated with sulphuretted hydrogen, allowed to stand, and filtered; the sulphuretted hydrogen is driven off by heat, and a current of chlorine is passed through the solution until the iron is completely transformed into the ferric salt; the excess of chlorine is driven off by a current of air in the ordinary manner. Finally, we make the volume up to 5 litres by adding pure hydrochloric acid.

The reagent and the hydrochloric acid are simultaneously assayed by distillation, by placing in the retort 15 grms. of ferrous sulphate free from arsenic.

IV. I have further found that this method, with a few slight alterations, may be applied to a large number of metals, such as irons and steels, lead, tin, zinc, &c., and to alloys, such as bronze, &c. It can be used for the detection and estimation of small proportions of arsenic which are frequently met with, or for the analysis of alloys or combinations in which arsenic is present in notable quantities. I propose to give more complete information on this subject in a future paper.—*Comptes Rendus*, vol. cxxvii., No. 4, July 25, 1898.

ON THE NATURE OF THE DIDYMIUM WHICH ACCOMPANIES THE YTTRIA OBTAINED FROM THE MONAZITE SANDS.

By G. URBAIN.

M. Boudouard recently announced that he had separated from the yttria of the monazite sands a didymium earth but slightly soluble in potassic sulphate, and presenting all the characteristics of neodymium.

I have pointed out in a previous note that the earth derived from the head crystallisations of the yttric ethylsulphates, entangle the didymium which had escaped the preliminary elimination of the earths of the ceric group by sulphate of potash.

I eliminated this didymium by fresh precipitations by sulphate of potash, and I noted that even if the didymium thus obtained had all the characteristics of neodymium, it could not be entirely identified with neodymium, and it also contained a large proportion of foreign earths.

The spectrum of this substance showed besides the bands of neodymium, the bands of M. Soret's X, also some bands of erbium and praseodymium. In all cases these bands were very faint. Some fractionations by sulphate of potassium in the presence of alcohol gave evidence of the presence of earths of the terbic group, and fractionation by ammonia in the presence of H_2O_2 sufficed to prove the presence of cerium. Thus this substance is actually very rich in neodymium, and I entirely agree with M. Boudouard when he recommends this new method as being likely to give better results than that adopted by M. Auer von Welsbach for the preparation of neodymium.

It is interesting to remark that among the bands of praseodymium that have been observed in this substance rich in neodymium, the band $\lambda = 469$ is distinctly visible, while the bands $\lambda = 444$ and $\lambda = 482$ are doubtful. M. Demarçay (*Comptes Rendus*, vol. civ., p. 580), and MM. Krüss and Nilson (*Deut. ch. Ges.*, vol. xx., p. 2134), made analogous observations on the variation of the relative intensities of these bands.—*Bull. Soc. Chim.*, Series 3, vol. xx., No. 9.

ON THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.*

Part I.

By JAMES LOCKE.

(Concluded from p. 70).

One of the pronounced features of the periodic system is the regularity with which the valency of the elements increases in the successive vertical rows—a regularity to which in fact so much importance is attached, that Mendeleeff can say without fear of criticism, "PbO_2 is the normal salt-forming oxide of lead, as are Bi_2O_5, CeO_2, TeO_3, of bismuth, cerium, and tellurium!" According to Mendeleeff, when an element forms two series of compounds, as copper, for instance, in one of which it has the same valency as its neighbour in the horizontal row, its compounds in this degree of oxidation must be similar to those of its neighbour. This rule is well illustrated in the case of copper, for the cupric compounds do bear a very close resemblance to those of the next element, zinc. But examine the rule in its full extension. The formation of an alum by any trivalent metal is rightly regarded as characterising its behaviour throughout all its compounds in this degree of oxidation, and sharply distinguishes its sesquioxide from those of another great class of elements, the rare-earth metals. Associated with the formation of alums is the behaviour of the cyanides toward potassium cyanide. All the sesquioxides† which form alums yield soluble double potassium cyanides, the great majority of which have the formula $K_3V(CN)_6$.

In the series—

K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni,

the most typical double cyanide is formed by iron; that of cobalt is also stable, and on the other side we find an analogous salt formed by manganese, "owing to its proximity to iron." But chromium, beyond manganese, also forms one; and from some experiments which I myself have made, I find also that potassium vanadicyanide, $K_3V(CN)_6$, is not only capable of existence, but a well-defined compound. We have here the character which the atomic weight 56 lends to the compounds of trivalent iron exerting an influence upon that of one element to the right and three elements to the left. With the alums the case is still more remarkable. These bodies are formed by cobalt, iron, manganese, chromium, vanadium, and titanium; or by six of the ten elements in a row. And not only that; scandium, the metal next to titanium, not only forms a sesquioxide, but this is its only degree of oxidation. Its compounds, however, have the properties characteristic, not of ferric and aluminium salts, but of the rare earths. And, nevertheless, the close proximity of

* From the *American Chemical Journal*, xx., No. 7.

† The only exception is in the case of aluminium, the cyanide of which is decomposed by water. Potassium cyanide precipitates the hydroxide.

this element to titanium does not lend to the trivalent compounds of the latter a single one of the properties of the rare earths. We must seek the influence to which their character is due far over at the edge of the table.

In the foregoing pages no attempt has been made to criticise the analogies which exist, in the various series, between the elements themselves. With this feature of the system, little fault can be found. The alkali metals, the alkaline earth metals, Be, Mg, Zn, .., Ge, Sn, Pb, are thoroughly similar among themselves, and well illustrate the gradation in properties with increasing atomic weight. But with the compounds the case is entirely different. The derivatives of typical elements show no regularity—even in their abnormal behaviour; the compounds of the 8th group have a decidedly anomalous position. The similarity between the derivatives of elements in states of oxidation uncalled for by the system, either cannot be explained at all, as in the case of lead and barium, magnesium and manganese compounds, or we are forced to ascribe to one or the other series a certain vague transitive nature. The reason for this lies, not in the principle that the chemical nature of an element and its compounds is a function of its atomic weight, but in our failure to recognise the two-fold character of this principle. We attempt to apply one and the same expression of the law to both elements and compounds. But one has no right, in the systematisation of one class of substances, to impose upon himself restrictions which arise only from the system which he employs for another class. No arrangement of the elements according to their atomic weights can be made which expresses the analogies between the elements themselves, and in which, for instance, magnesium and manganese receive analogous positions. And the result is that, in order to emphasize the relation between zinc and magnesium which such an arrangement does exhibit, the adherent of the periodic system deliberately closes the door to an explanation of the far closer analogy between the compounds of magnesium and manganese, as if the latter were not conditioned by an equally important law of nature.

A system for the compounds, founded upon the atomic weights of the elements must also necessarily lead to confusion from another source, for the investigation of the compounds is undertaken solely to characterise the *general chemical nature* of the element. Thus, little distinction is drawn between reactions which do not involve a change in the degree of oxidation and those which do. If the two are separated at all, it is only when the resulting compounds are very stable, or else conform to the position of the element in the periodic system. To cuprous compounds, though they are unstable, great importance is attached, because copper belongs to the first family. But, even in so full and scientific a text-book as that of Mendeleeff, the salts of trivalent manganese are reviewed with little more than the passing remark that they somewhat resemble ferric compounds, and that the chloride decomposes when its solution is warmed. The latter fact seems to deprive the manganic salts of all theoretical interest.

But in a comparison between the derivatives of two metals in the same degree of oxididation, the question of *existence* becomes of more importance than stability, for the latter is often dependent entirely upon external conditions. The fact that bromine is liquid, iodine a solid, at ordinary temperatures, does not prevent the most important analogies being drawn between the physical properties of the halogens in the same state of aggregation, though to obtain bromine and iodine as gases, heat must be employed. So it is with many compounds. They may perhaps be obtained only under, for us, extraordinary conditions, but their very existence may point out in the constituent elements properties which we should otherwise never expect. As an example of such a case only the newly discovered alums of vanadium need be mentioned. The existence of these bodies shows that in spite of the similarity between phosphates and vanadates, the vanadium atom exerts upon the nature of its trivalent compounds the same influence as does iron upon that of the ferric salts. A vanadic solution absorbs oxygen with great avidity, and is therefore called very unstable, but the presence of oxygen is an arbitrarily imposed condition. If oxygen were a rare element, the trivalent salts of vanadium would probably be regarded as its normal compounds, and a vanadate looked upon very much as we look upon ferric acid to-day.

The chemical behaviour of an element in a given degree of oxidation must be characterised along two lines. First, by the study of its compounds as mineralogical specimens, their composition, physical properties, solubility, volatility, and the like, together with the reactions which they show without involving change in the degree of oxidation. Secondly, by its passage from this degree of oxidation into others. The first is, in my opinion, by far the more important, for the properties of the compounds of an element in two different degrees of oxidation differ absolutely from one another; and in the two the element appears in entirely different rôles. It is only after we have ascertained in how far the element can alter its *apparent* character, in corresponding with entirely different elements in different degrees of oxidation, that we can solve its *true* character, and find out a general law for its behaviour in all its compounds; and this can be ascertained only by a careful comparison of its compounds with those of other elements in the same degree of oxidation.

A classification based upon this principle, of course, presents great difficulties, owing to the very unsatisfactory extent to which the elements in their unstable degrees of oxidation have been investigated. A thorough study of the compounds, however, has shown that it is capable of giving most interesting results, the nature of which I will discuss in my next article on the subject.

PRELIMINARY REPORT OF THE COMMITTEE ON COAL ANALYSIS.*

At the Cleveland meeting of the American Chemical Society a Committee, consisting of W. F. Hillebrand, C. B. Dudley, and W. A. Noyes, was appointed to consider the methods of proximate analysis of coal with a view to the adoption, if possible, of uniform methods for this country. After discussion among themselves, the committee have formulated the following outline of methods for analysis which they herewith submit, rather as a means of securing further information than as a final report. The committee very earnestly request all chemists interested in the matter, who may see this report, to send to the chairman of the committee a criticism of the methods proposed and a statement of any objections they see, and of any modifications which they think desirable.

Since the literature of the subject is widely scattered and much of it is not easily accessible, the committee request that all who have published papers bearing on the subject will, if possible, send to the committee reprints of such papers, or, if that cannot be done, a statement of where such papers can be found and the points covered.

Without the full and hearty co-operation of others, the labours of the committee will be greatly increased, and the conclusions finally arrived at will be less representative of general experience than it is desired they should be.

Methods of Analysis.

1. *Sampling.*—At least 5 pounds of coal should be taken for the original sample, with care to secure pieces that represent the average. These should be broken up and quartered down to obtain the smaller sample which is to be reduced to a fine powder for analysis. The quartering and grinding should be carried out as rapidly

* From the *Journal of the American Chemical Society*, xx., No. 4.

as possible, and immediately after the original sample is taken, to prevent gain or loss of moisture. The powdered coal should be kept in a tightly stoppered tube or bottle till analysed.

2. *Moisture.*—Dry 1 grm. of the coal in an open porcelain or platinum crucible at 104—107° for one hour, best in a double-walled bath containing pure toluene. Cool in a desiccator and weigh covered.

Question: Has anyone experience with other methods of drying? over sulphuric acid, *in vacuo*, in a current of air, in watch-glasses, or otherwise? Especially in this and other cases the committee desire any comparative results which can be furnished.

The following comparison of the effect of drying one hour in toluene bath, twenty hours *in vacuo* over sulphuric acid, and in air over sulphuric acid was made by Dr. Hillebrand.

	One hour in toluene bath.	Twenty hours *in vacuo* over H_2SO_4.	In air over H_2SO_4. 2 hrs.	48 hrs.	120 hrs.
Coal No. 1 ..	2·85	3·60	2·87	3·15	3·39
,, ..	3·10	3·59	—	—	—
,, ..	3·23	3·57	—	—	—
,, ..	3·25	3·49	—	—	—
,, ..	3·24	—	—	—	—
,, ..	3·22	—	—	—	—
,, ..	3·27	—	—	—	—
Coal No. 2 ..	1·84	2·08	1·77	—	2·00
,, ..	1·83	2·07	—	—	—
Coal No. 3 ..	1·52	1·75	1·42	—	1 70
,, ..	1·51	1·73	—	—	—
Coal No. 4 ..	1·01	1·04	1·05	—	1·18
,, ..	1·08	1·03	—	—	—
Coal No. 5 ..	1·40	1·69	1·45	—	1·66
,, ..	1·41	1·67	—	—	—
,, ..	—	1·67	—	—	—
Coal No. 6 ..	0·30	0·21	0·23	—	0·25
,, ..	0·34	0·28	—	—	—

These results seem to indicate that drying *in vacuo* gives higher, and probably more correct, results than drying at 105° for one hour.

The following experiments were carried out by Mr. W. E. Burk at the Rose Polytechnic Institute (see *Proc. Indiana Acad. of Sciences*, 1896, p. 113) for the purpose of determining whether volatile matter other than water is lost in drying bituminous coals. A hard glass tube was partly filled with copper oxide, partly jacketted with a glass sleeve so that a portion could be heated to 100° by a current of steam. The coal was weighed in an aluminum boat enclosed in a weighing tube, and was then heated to 100° for an hour in a current of dry air. The moisture and any volatile matters which were expelled were passed over the heated copper oxide and the water and carbon dioxide were absorbed as usual in calcium chloride and in potash bulbs. The results were as follows:—

Weight of coal taken.	Loss in weight of coal at 100°.	Water found in calcium chloride tube.	Per cent of water in coal.	Per cent of carbon found in potash bulbs.	Per cent of excess of hydrogen found.
1·4217	0 1994	0·2014	14·00	0·048	0·016
1·1195	0·1596	0·1625	14·25	0·058	0·029
3·1079	0·2111	0·2113	6·78	0·022	0·001
3·2356	0·2152	0·2142	6 65	0·025	—
2·9408	0·1967	0·1967	6·65	0·037	—

The amount of moisture found was slightly higher than was found in the same coal by the usual method, perhaps because of the current of dry air over the coal. Since the loss of volatile matter other than water was always less than one-tenth per cent, it can safely be disregarded for most practical purposes with coals of this class.

3. *Volatile Combustible Matter.*—Place one grm. of fresh undried coal in a platinum crucible, weighing 20 to 30 grms. and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 c.m. above the top of the burner. The flame used should be 20 to 25 c.m. high when burning free, and the determination made in a place free from draughts. The upper service of the cover should burn clear, but the under surface should remain covered with carbon. To find "Volatile Combustible Matter," subtract the per cent of moisture from the loss found here.

Questions: Should a larger portion be taken? Should the coal be heated more gradually at first? Should a blast be used? Can results be obtained by heating in a muffle, or in any other manner, which will agree with those obtained by this method?

The committee consider the determination as largely arbitrary, in any case, and believe that uniform results in the hands of different chemists will be best secured by making the conditions as simple as possible. The most serious objection to the method proposed appears to be the danger of mechanical loss at the commencement of the heating. It is believed, however, that the error from this source is less than would arise from any method which leaves the application of the heat to the judgment of the operator.

The committee especially desire to secure any analytical data which may be available to show the degree of concordance of results obtained by the same or different chemists, Also any comparison of analytical results with results of commercial coking.

4. *Ash.*—Burn the portion of coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter.

Question: Are carbonates likely to be present in the ash in such amount that heating over a blast would lessen the weight appreciably?

When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of the ash, and, since three atoms of oxygen replace four atoms of sulphur the weight of the ash is less than the weight of the mineral matter in the coal by five-eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee is not now prepared to recommend such a correction.

5. *Fixed Carbon.*—This is found by subtracting the per cent of ash from the per cent of coke as found in paragraph 3.

6. *Sulphur.*—What methods are used? Eschka's, with sodium or potassium carbonate, fusion with sodium carbonate and potassium nitrate, Carius's or others? Any comparative results are especially desired.

7. The committee would recommend that the heating effect be calculated on the basis of the coal burned to carbon dioxide and vapour of water at 100° C., and be stated either in calories per kilogrm. or English heat units per pound. The theoretical evaporative effect is to be calculated by dividing the number of calories per kilogrm. by 536, or the number of English heat units per pound by 965. In either case it expresses the theoretical number of kilogrms. or pounds of water converted into steam from and at 100° C. by one kilogrm. or pound of the coal.

A calculation of the results of 21 analyses, and determinations of heating effect with the bomb calorimeter, made with Indiana and Pittsburg bituminous coals, shows that the heating effect may be found in all cases examined, with a maximum error of 2 per cent, by the following rule:—

Subtract from 100 the per cents of moisture and ash and one-half the per cent of sulphur, and multiply the remainder by 80·7. The product will be the heating effect of the coal burned to vapour of water, expressed in calories.

The committee will be glad of any data which will

enable them to further test this factor, and also of any data with regard to other methods of determining heating effect.

Persons interested in the subject of coal analysis are requested to send any communications they may wish to make to Prof. W. A. Noyes, Rose Polytechnic Institute, Terre Haute, Ind.

W. A. NOYES,
C. B. DUDLEY,
W. F. HILLEBRAND, } Committee.

February 22, 1898.

A REDUCTION OF PERMANGANIC ACID BY MANGANESE PEROXIDE.*

By H. N. MORSE and C. L. REESE.

IN a previous article (*Am. Chem. Journ.*, xviii., 401), one of us, together with Messrs. Hopkins and Walker, described certain experiments on the reduction of permanganic acid by percipitated manganese peroxide. It was there concluded that, whenever the latter is introduced into, or is formed in the presence of, the former or its salts, a reduction of the acid occurs with an evolution of three-fifths of its active oxygen, in accordance with the following equation—

$$x\mathrm{MnO_2} + 2\mathrm{HMnO_4} = (x + 2)\mathrm{MnO_2} + \mathrm{H_2O} + 3\mathrm{O}.$$

It was also shown that to this cause is to be ascribed the observed instability of solutions of permanganate.

Six months later (*Ber. d. Chem. Ges.*, xxix., 2549), there appeared an article by Messrs. V. Meyer and Max Von Recklinghausen in which is described the evolution of oxygen which takes place when hydrogen or carbon monoxide is absorbed by a nearly saturated (5 per cent) acidified solution of potassium permanganate. The opinion was then expressed by one of us (*Ibid.*, xxx., 48), that the phenomenon observed by Messrs. Meyer and Von Recklinghausen was due to the peroxide which is formed when reducing gases are absorbed by permanganic acid; in other words, that it is an instance of a kind of reaction which had been under observation in this laboratory for several years.

After the communication referred to had left the hands of the author, but before it appeared in printed form, an article by Messrs. H. Hirtz and V. Meyer was published (*Ber. d. Chem. Ges.*, xxix., 2828), in which they maintain that the phenomenon observed by Messrs. Meyer and Von Recklinghausen is fundamentally different from that described by Morse, Hopkins, and Walker. The grounds for this opinion appear to be two-fold. In the first place the authors make the wholly unwarranted assumption that Morse, Hopkins, and Walker experimented with *neutral* solutions only, that is, with potassium permanganate; while Messrs. Meyer and Von Recklinghausen employed *acidified* solutions. We cannot interpret otherwise the expressions: "Diese Forscher haben gefunden dass eine Loesung von uebermangansaurem Kali unter gewissen Bedingungen durch fein vertheilten Braunstein unter Entwickelung von Sauerstoff zersetzt wird." . . . "Da nämlich Wasserstoff und Kohlenoxyd als reducirende Koerper aus der Loesung der uebermangansäure Braunstein ausscheiden, und dieser, nach den genannten Autoren, mit Kaliumpermanganat Sauerstoff unter gewissen Bedingungen entwickeln kann." . . . "Ob nun die Morse-Hopkins-Walker'sche Erscheinung bei unseren *Säure*-loesungen eintrete." . . . How erroneous must have been the view which we ascribe to Messrs. Hirtz and Meyer, on the basis of the above quotations, will appear when we state that, of the forty-eight experiments described by Morse, Hopkins, and Walker, thirty-five were with *acidified* solutions of permanganate.

The second ground which the authors have for believing that the evolution of oxygen observed by them is not due to the action of the oxide on the permanganic acid, is one of great weight, but, to our minds, it is by no means conclusive. They found that when hydrogen, or carbon monoxide, is absorbed by a 5 per cent solution of potassium permanganate to which has been added 2·5 volume-per cent of concentrated sulphuric acid, the evolution of oxygen which occurs *during the absorption* is much more rapid than that which takes place *after the exhaustion* of the gas. This was shown in the following manner: 20 c.c. of the acidified permanganate solution and 40 c.c. of hydrogen were inclosed in a glass-tube and agitated together for twenty-four hours. The tube was then opened and the gas in it displaced by carbon dioxide. On closing the tube again and agitating the contents for another twenty-four hours it was found that only 2·5 c.c. of oxygen had been liberated, whereas, according to the experience of Messrs. Meyer and Von Recklinghausen, about 20 c.c. of oxygen are evolved when, under similar conditions, 20 c.c. of the permanganate solution and 40 c.c. of hydrogen are agitated for the same length of time, or even for a shorter time.

It is clear then—and our own results, to be given hereafter, confirm the conclusion—that the evolution of oxygen, which occurs when a gaseous reducing-agent is being absorbed by a concentrated acidified solution of permanganate, is much more rapid than that produced by the oxide, which results from the absorption after the gas has disappeared. It is also more rapid than that observed when an equivalent amount of oxide is produced in the permanganic acid by a liquid reducing-agent, like a solution of manganous sulphate. To us, however, the conclusion that the evolution of oxygen in the two cases is due to wholly different causes is not obvious. We should suspect, rather, that the great initial evolution, observed when hydrogen and carbon monoxide are absorbed, is in some way dependent on the *gaseous* character of these reducing-agents.

We know at present altogether too little regarding the reduction of permanganic acid by the peroxide to give an opinion of any value as to its cause; and we attach very little value to present speculations on the subject, except so far as they may prove useful in giving direction to a further study of the phenomenon. There is, however, one fact which suggests a provisional hypothesis. We have considerable evidence tending to show that the molecules of the ordinary precipitated peroxides of manganese are quite complex. Perhaps the best evidence of this is to be found in the large formulæ which must be assigned to them in view of the small proportions of water, or of alkalis or other bases which they contain. If they are thus complex, it is conceivable that the tendency toward increasing complexity of constitution should be strong enough to effect the decomposition of permanganic acid with liberation of the superfluous oxygen.

If, in the absence of any other explanation the reduction of permanganic acid by the peroxide, we accept for the moment the proposed hypothesis, we should ascribe the greater inital evolution of oxygen which is observed when gaseous re ducing-agents are used, to the greater initial simplicity of the precipitated peroxide molecules. It is interesting in this connection to notice the volume-relations of the hydrogen absorbed and the oxygen which is liberated during or immediately following the absorption. They are approximately 2 : 1 in all of the experiments of Meyer and Von Recklinghausen. This relation would be explained in terms of the suggested hypothesis by the following reactions:—

$$2\mathrm{HMnO_4} + 3\mathrm{H_2} = 4\mathrm{H_2O} + 2\mathrm{MnO_2};$$
$$2\mathrm{MnO_2} + 2\mathrm{HMnO_4} = \mathrm{H_2O} + 2(\mathrm{MnO_2})_2 + 1\tfrac{1}{2}\mathrm{O_2}.$$

We wish to state again that we have but little confidence in the above speculations. We claim for this merit only, that, inherently, they are not less improbable than the supposition that the evolution of free oxygen in the two cases under consideration is due to entirely distinct and different causes.

* From the *American Chemical Journal*, xx., No. 7.

Furthermore, we do not see that the problem can be solved by any simple experimental demonstration. The "experimentum crusis" of Messrs. Hirtz and Meyer (*Ber. d. Chem. Ges.*, xxix., 2829), established but one thing; namely, the fact that the evolution of oxygen is phenomenally rapid during or immediately subsequent to the precipitation of the peroxide when a gaseous reducing-agent is employed, and that fact, taken alone, appears to throw no light on the cause of the evolution. Convinced that, with our slight bases of established fact, discussion is premature, if not profitless, we have undertaken a further study of the reduction of permanganic acid by manganese peroxide. The present communication contains the results which were obtained on treating the acid, under equal conditions, with equivalent quantities of hydrogen gas and manganous sulphate. We have thus far experimented with three concentrations of permanganate solution.

The first (A) contained in 1 c.c. 2·822 miligrms. of $KMnO_4$ equivalent to 5 milligrms. of iron. The second (B) was twice as concentrated as A. The third (C) contained in each c.c. 51 milligrms. of $KMnO_4$, equivalent to 90·38 milligrms. of iron. The solutions A and B are of the concentration usually employed in analytical work, while C has about the strength of the 5 per cent solution which was employed by Messrs. Meyer and Von Recklinghausen and later by Messrs. Hirtz and Meyer.

Great pains were taken to free these solutions from the oxide which is usually found in the commercial salt, and which, as has been shown, is the usual cause of the instability of unfiltered solutions of potassium permanganate. To this end compact abestos filters were prepared upon perforated porcelain disks placed in the bottom of cylindrical funnels, such as are used in the Gooch method of filtration. Two filters, one placed above the other, were employed. The lower one was closed with a perforated stopper through which the stem of the upper one passed. The filter through which the liquid entered the flask was thus protected from the dust of the air, and the absence of any brown colouration of the lower filter proved the effectiveness of the filtration. We have found these precautions necessary in all quantitative experiments on the reduction of permanganic acid by the peroxide; since, if they are neglected, it is impossible to ascertain how much of the observed reduction is to be ascribed to the oxide purposely added, and how much to that which was already in the solution.

When solutions of permanganate which contain suspended oxide are heated—especially those which have been acidified—the quantity of the oxide increases very rapidly. We call attention to this fact in connection with the necessity for careful filtration, because it appears to us to have a bearing on some of the results which were obtained by Messrs. Meyer and Von Recklinghausen. Their acidified solutions were "gut ausgekocht," but it does not appear from their published account that they were filtered.

The volume of permanganate solution used was the same in all experiments; namely, 20 c.c. This quantity was enclosed with whatever was to be added to it, in tubes having about 80 c.c. capacity, except in the case of solution C, where, owing to the large volume of hydrogen used in some experiments, larger tubes were employed.

Our agitating arrangement was an oscillating table upon which the tubes were held by rawhide lacings. The table was rocked by means of an electric motor and made about 100 strokes per minute. The agitation was continuous, except for occasional interruptions which lasted only a few minutes.

The amount of reduction effected during the agitation was measured by means of standard solutions of oxalic acid and potassium permanganate. This method, with the use of calibrated measuring apparatus, appeared to us quite as accurate as that of determining directly the volume of the liberated oxygen.

Messrs. Meyer and Von Recklinghausen found that when 20 c.c. quantities of their 5 per cent acidified solution of permanganate were agitated with air in closed tubes, they obtained volumes of oxygen ranging from 1·9 to 2·9 c.c. An agitation of thirty-three and a half hours gave them 1·9 and 2·2 c.c., while in a parallel experiment in which the agitation was continued for eighty-seven hours they obtained only 2·4 c.c. In another instance the volumes of liberated oxygen were, at the end of thirty-three and a half hours 2·8 and 2·9 c.c., and at the end of eighty-seven hours 2·4 c.c. Since the decomposition was not appreciably greater in eighty-seven than in thirty-three and a half hours the authors were led to believe that there is a limit to the reaction by which the oxygen is liberated. These results were not in accord with our own experience. In the first place, we have always found dilute, moderately acidified solutions of permanganate quite stable at ordinary temperatures, provided they were free from oxide. In the second place, in all the cases which have come under our observation, the decomposition of permanganic acid by the peroxide, which is attended by the liberation of oxygen, has been a continuous reaction, which ceased only when all of the acid had been reduced to the oxide. We had not, however, experimented with solutions as concentrated as that used by Messrs. Meyer and Von Recklinghausen. We therefore inclosed in glass tubes of about 80 c.c. capacity 20 c.c. portions of permanganate solution C. (51 milligrms. of $KMnO_4$ per c.c.) and volumes of diluted sulphuric acid, which were equivalent to three times the potassium of the salt. These were agitated for twenty-four hours and then titrated with oxalic acid. The reduction, if any had taken place, was too minute to be detected, nor was any trace of a brown deposit upon the glass to be discovered. The degree of acidity was somewhat greater in our solution than in that employed by Messrs. Meyer and Von Recklinghausen. The difference in the results we must ascribe to the absence of oxide from our solution, and the presence of it in theirs. Their 5 per cent solution of permanganate was acidified with *concentrated* acid, and then boiled ("gut ausgekocht"), but it does not appear to have been filtered. This treatment leads infallibly to the formation of a large quantity of the oxide; for, when strong sulphuric acid is added to a 5 per cent solution of the salt, there is a visible precipitation of the peroxide, and the quantity of it is rapidly increased by heating the solution to the boiling-point. Our solution, on the other hand, was filtered with great care, and acidified with diluted acid (3 parts of water to 1 of acid). Moreover, great pains were taken in cleansing the tubes, and to prevent the entrance into them of dust, or any reducing substance.

Having failed to establish the fact of decomposition within twenty-four hour periods, we determined to extend the time of agitation, using varying proportions of acid; and to compare the more dilute solutions A and B with C with respect to stability. The results, and the conditions under which they were obtained, are given in tabular form. The numbers given under the head of "volume reduced" signify reduction in accordance with the equation $2HMnO_4 = H_2O + 2MnO_2 + 3O$, and not total reduction of the permanganic acid. (See next column).

It will be seen that none of the three solutions in the neutral condition lost a measurable quantity of oxygen. As regards the acidified solutions, it appears that A and B suffered but little, if any, decomposition, whether the acid was equivalent to once or six times the potassium of the permanganate. In the case of those acidified portions of the solution C, in which the acid was equivalent to three times the potassium of the permanganate, there was, after an agitation of one hundred and fifty hours, some evidence of decomposition. A slight deposit of the brown oxide could be detected upon the glass. This evidence of reduction was wanting in those instances in which the acid was equivalent to once and twice the potassium.

If we succeeded in our endeavour wholly to exclude the oxide from our solutions, it must be concluded that a 5 per cent solution of permanganate becomes *per se* some-

Acid.	Time. Hours.	Volume reduced. C.c.	Oxygen lost. C.c.
Permanganate Solution A ; 1 c.c. = 5 M.grms. Fe.			
O	300	0·12	0·06
O	300	0·11	0·05
=K	300	0·11	0·05
=K	300	0·06	0·03
=2K	300	0·20	0·10
=2K	300	0·10	0·05
Permanganate Solution B ; 1 c.c. = 10 M.grms. Fe.			
O	150	0·02	0·02
O	150	0·04	0·04
=3K	150	0·10	0·10
=3K	150	0·10	0·10
=6K	150	0·08	0·08
=6K	150	0·10	0·10
Permanganate Solution C ; 5 per Cent $KMnO_4$.			
O	150	0·00	0·00
O	150	0·00	0·00
=K	150	0·05	0·45
=K	150	0·04	0·36
=2K	150	0·02	0·18
=2K	150	0·11	0·99
=3K	150	0·40	3·61
=3K	150	0·22	1·91

what unstable when treated with a quantity of sulphuric acid which is equivalent to three times the potassium of the salt. Our solution C, however, proves itself much more stable than the equally concentrated, but somewhat less acid, solution of Messrs. Meyer and Von Recklinghausen. The most obvious cause of this difference we have already referred to, namely, the certain presence of suspended oxide in their solution at the beginning of the agitation.

We shall not attempt to explain the fact that Messrs. Meyer and Von Recklinghausen obtained no larger volumes of oxygen after an agitation of eighty-seven hours than were liberated in other experiments during thirty-three and a half hours; but it occurs to us as something which may have a bearing on the case, that unless proper precautions were taken at the time of transferring the liquid to the tubes, to secure a uniform distribution of all the suspended and precipitated oxide, the quantities of oxide introduced into the different tubes would be likely to vary. That the liberation of oxygen, which occurs when an acidified solution of permanganate containing suspended oxide, is agitated in closed tubes, *does not* cease after a few hours will be amply proved by our later experiments.

(To be continued).

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 66).

Silica, Alumina, &c.

Remarks on alternative Methods of Decomposition.—Various fluxes other than alkaline carbonates have been recommended for breaking up silicates insoluble in ordinary acids, such as lead and bismuth oxides, lead carbonate, borax, and boric acid. Prof. P. Jannasch and his pupils have been especially active of recent years in this line of work, as evidenced by their numerous published papers. One of the advantages these fluxes possess over the alkaline carbonates is their removability after serving their purpose, thus allowing the various separations to be made more perfectly and without the annoying interference of several grms. of foreign fixed salts, which are most troublesome in that part of the analysis devoted to the separation of silica, alumina, iron, lime, and magnesia.

Another of their advantages is that with some of them it is possible to estimate in one portion the alkalies, in addition to those constituents usually determined in the silica portion. Where the material is limited, as it so often is in mineral analysis, this is a most important advantage, sufficient to outweigh all possible objections; but in rock analysis, where the supply of material is usually ample, it is rarely worth considering. A still further point in their favour is, that it is probably more easy to obtain them entirely free from fixed impurities than an alkaline carbonate.

There are, however, objections to their use. With some of them an extraordinary amount of time must be devoted to grinding the mineral to an impalpable powder, and the flux itself may need considerable hand pulverisation. Once introduced, they must be removed before the analysis can be proceeded with, and this removal takes much time and is always a possible source of error. The expulsion of boric acid and drying of the silica in the recent method of Jannasch and Heidenreich (*Zeitsch. fur Anorg. Chemie*, xii., p. 208, 1896), from their own account requires the almost constant supervision of the chemist for several hours. In mineral analysis these objections are entitled to far less weight than in rock analysis, since the object sought—usually the deduction of a formula—warrants the expenditure of much time and painstaking care. Finally, it has been found that one or more of these fluxes are not available for altogether general use, since certain minerals do not fully succumb to their attack, as andalusite with boric acid and others with lead oxide (Jannasch). Therefore, however well adapted one or the other of these methods may be for the analysis of homogeneous minerals, it is very improbable that the vivid anticipations of Prof. Jannasch (*loc. cit.*, p. 219), to the effect that the boric-acid method will soon supersede the alkaline-carbonate-fusion method in rock as well as mineral analysis, will be speedily realised. Nor can the great saving in time of 50 per cent which is claimed be for a moment admitted. It may be that a chemist attending to only one analysis at a time will finish it somewhat sooner by following Prof. Jannasch's procedure than the one here outlined; but it is quite possible, as previously intimated, for two—or even sometimes portions of three—analyses to be carried on in different stages of completion at the same time by the methods herein set forth.

The practice of separating alumina, &c., by the usual methods, after first attacking the rock powder by hydrofluoric and sulphuric acids—silica being estimated in a separate portion—while attractive in principle, was abandoned by the writer after fair trial, owing to the disturbance sometimes occasioned by incomplete expulsion of fluorine and to a less degree by the presence of sulphates instead of chlorides. With exception of the comparatively few analyses made thus, the sodium-carbonate method has always been employed. In the case of rocks rich in fluorine strict accuracy would require the separation of silica to be made as in the Berzelian method for fluorine estimation; but in practice it is hardly ever necessary to resort to this tedious procedure, since the amount of fluorine is usually small, and it can by no possibility cause a loss of much more than three-fourths its own weight of silica by volatilisation as silicon fluoride when the sodium-carbonate fusion is evaporated directly with hydrochloric acid. Probably the loss is less, since some fluorine perhaps escapes as hydrofluoric acid. However this may be, the error is of comparatively slight importance, since it attaches to the constituent always present in greatest amount.

Purity of the Sodium Carbonate used as a Flux.—Notwithstanding the most earnest efforts for years, it has been impossible to procure, either in the open market or

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

by special arrangement with manufacturers, an article of sodium carbonate which can be called chemically pure. With special precautions small lots can be prepared in the laboratory that will contain less than 1 m.grm. total impurity in 10 grms.; but such an article cannot be purchased in the market, and rarely will the so-called chemically pure dry sodium carbonate contain as little as 1 m.grm. in 10 grms. The invariable contamination, aside from sand and straw, which have sometimes been found in large amount, is silica, alumina, iron, lime, and magnesia, all of these going into aqueous solution with the carbonate. The chief of these impurities are usually silica, alumina, and lime. An article of the above degree of purity is satisfactory in almost all imaginable cases, since the use of the usually extravagant amount of 10 grms. for a fusion would introduce an error of but 0·1 per cent in the analysis, supposing 1 grm. of mineral to be operated on. This error is undoubtedly fully equalled by the introduction of dust from the air in the various long evaporations.

Precautions in Fusing.—Special directions with regard to the fusion and its first treatment are unnecessary, except to say that the flame should not be directed vertically against the bottom of the crucible, but at an angle against the side and bottom, nor should the flame be allowed to envelop the whole crucible. These precautions apply in all ignitions of reducible substances, and yet they are rarely observed. In neither case, if neglected, will there be the necessary oxidising atmosphere within the crucible; on the contrary, reduction may occur fraught with serious consequences. This is especially true if the rock contains more than traces of pyrite or other sulphide, when, after cleansing and igniting the crucible, there may appear on its interior a darkening due to oxidation of reduced iron which had alloyed with the platinum. This may in exceptional cases amount to several m.grms. in weight, and can be removed only by repeated ignitions, followed each time by scouring or treatment with hydrochloric acid. In order to avoid the use of nitre in case of pyritiferous rocks, it is well to first roast the weighed powder in the crucible in which the fusion is to be made.

It sometimes happens that the cooled flux, and even its solution, will indicate absence of manganese when it is really present in quantity to give normally a strong colouration. Two fusions made side by side or successively, under apparently similar conditions, may in one case show little or no manganese; in the other considerable. This observation has been frequently made, and therefore the absence of a bluish-green colour in the fusion is not to be taken as proof of the absence of manganese. This difference of behaviour I can ascribe to no other cause than that of a reducing atmosphere in one of the crucibles and an oxidising one in the other, even though the conditions were apparently alike.

Drying and Testing of Silica.—As to the best way of rendering silica insoluble by evaporation, my own predilection is for a double evaporation instead of a single one on the water-bath. By fusing with sodium carbonate in the forenoon, the silica is ready for the first filtration in the afternoon. It is quite unnecessary to carry the evaporation beyond approximate dryness. The filtrate is again evaporated, always in platinum, and is ready for final filtration the following morning, when approximately 1 per cent of silica is recovered and added to the main portion. My experience is that a better separation of silica is effected hereby, and in no more time than by a single long evaporation. That which is subsequently recovered from the ammonia precipitate rarely exceeds a half, or, at the most, 1 m.grm.

Drying in an air-bath at 110° C. or higher, or on a hot plate or sand-bath, or over a free flame, in order to render silica insoluble, offers no advantage unless much magnesium is present, and then the most favourable temperature, according to Gilbert (*Technology Quarterly*, iii., p. 61, 1890; Abstract in Fresenius's *Zeitschr. fur Anal. Chemie*, xxix., p. 688, 1890), is 120° C. The presence of much calcium chloride seems to facilitate dehydration of the silica, while magnesium chloride above 120° C., by decomposing, forms a silicate which dissolves in hydrochloric acid and increases the amount of silica carried into the filtrate. It does not appear from Gilbert's paper that the blast-furnace slags, on which he experimented, contained titanium, phosphorus, or iron in appreciable amounts. Basic magnesian rocks usually do, and in such cases it is doubtful if the employment of a drying temperature of 120° would not materially add to the large impurity always to be expected with the silica. In other cases he confirms the earlier belief that drying temperatures higher than that of the water-bath increase the amount of insoluble impurity, chiefly alumina, in the silica, and that this amount cannot be reduced by long digestion with hydrochloric acid. Further, he confirms Lindo's statement that evaporation with sulphuric acid till the appearance of white fumes gives a higher result in silica than with hydrochloric acid. But for general rock analysis the use of sulphuric acid at this stage must be rejected utterly.

Blasting for twenty to thirty minutes is necessary to expel all moisture from the silica. Its weight should always be corrected for impurities, which are never absent, by evaporating with hydrofluoric and sulphuric acids and again blasting. If toward the end of evaporation with these acids, when the hydrofluoric acid has been driven off and the sulphates begin to appear in solid form, the residue has a peculiar milky or enamel-like appearance, it may be taken as evidence of much phosphorus and titanium.* This appearance is so unusual and striking that it is worth while calling attention to it. With basic rocks very rich in titanium and phosphorus the residue may amount to 2 or even 3 per cent of the rock.

The subsequent precipitate of alumina, &c., is usually ignited in the crucible containing the residue from the silica.

It might be supposed that this residue would contain most of the barium of those rocks carrying that element together with sulphur or sulphates, but the reverse is true as a rule. Only when there is a considerable excess of SO_3 over the BaO will much of the latter be found there, and usually there is none at all. Should some be present, its removal and estimation at this stage is not necessary, as it can be more conveniently recovered later, together with the silica accompanying the alumina, &c., precipitate.

The separation of silica in rocks containing fluorine has been touched upon in commenting on the sodium carbonate method of fusion.

Platinum in Filtrates.—The filtrates from the silica always contain notable amounts of platinum. This arises in very small degree from the crucible fusion, in a larger one from the action of hydrochloric acid on manganate and permanganate, sometimes chromate of sodium, and, if much iron is present, in no small degree from the reduction of ferric chloride to ferrous by the platinum of the dish. This reaction is little known, apparently, but is mentioned in Gmelin-Kraut (*Anorg. Chem.*, iii., p. 359, sixth revised edition), and can be readily demonstrated by evaporation of ferric chloride in platinum.

Metals of the Hydrogen Sulphide Group.—The presence in appreciable amounts of metals precipitable by hydrogen sulphide, except perhaps copper, is of such infrequent occurrence in most rocks that discussion is unnecessary in their connection. In case it is necessary to precipitate them, however, it is always well to bear in mind that some titanium may be thrown down along with them. Separations of the silica should be made in porcelain, to eliminate platinum, or, better still, the quantitative estimation of any of these metals should be made in a separate

* It is possible that this appearance is caused by zirconium with the phosphorus and titanium. (See page 81, footnote).

portion of the rock broken up by the action of hydrofluoric and sulphuric acids.

Alumina, &c.—The removal of platinum from the filtrates before precipitating alumina and iron is quite unnecessary, and to do so would involve the re-oxidation of all iron and subsequent boiling to remove or destroy the excess of oxidising agent, together with the waste of much valuable time. The iron is already oxidised by the fusion, and needs no further help in that direction.

Two precipitations by ammonia are usually quite sufficient to separate iron, alumina, phosphoric acid, chromium, titanium, and zirconium, if all these are present, from nickel, manganese, the alkaline earths, and magnesium, provided ammoniacal salts are present in sufficient quantity. This last point is of special importance as regards magnesium, and failure to observe it is doubtless the reason why many old analyses and sometimes modern ones show utterly improbable percentages of alumina, especially as chemists were formerly often satisfied with a single precipitation. The necessary ammonium chloride is better obtained by the use of purified ammonia water and hydrochloric acid than by the addition of the solid salt, which is seldom pure.

Manganese not always separated by Ammonia.—But it will occasionally happen that the separation from even very small amounts of manganese is altogether incomplete, and the uncertainity of insuring this separation has led the writer of late to employ the basic acetate method for the first precipitation in all cases where manganese is present—and the exceptions are few—even though the precipitation of alumina is sometimes less complete than by ammonia.* Not more than 2, or at most 3, grms. of sodium acetate need be used. After slight washing the precipitate is re-dissolved in a sufficient excess of hydrochloric acid and re-precipitated by ammonia in slight excess. The complete boiling off of this excess is unnecessary, as pointed out by Genth and Penfield, since it is apparently the washing with pure water and not the free ammonia which carries small amounts of alumina into the filtrate. Penfield and Harper (*Am. Journ. Sci.*, Series 3, vol. xxxii., p. 112, 1886), recommend washing with a dilute solution of ammonium nitrate (20 c.c. nitric acid, neutralised by ammonia, to the litre), and also the solution of the first precipitate in nitric instead of hydrochloric acid, in order to shorten the washing, there being no chloride to remove.

The filtrates are strongly concentrated separately† in platinum, a drop or two of ammonia being added toward the end to the second one, and filtered successively through the same small filter into a flask of 150 to 200 c.c. capacity, the ammoniacal filtrate serving as wash water for the first dish and containing enough ammoniacal salt to prevent precipitation of magnesium in the first filtrate when mixed with it. If manganese has been deposited upon the surface of the dish it is removed by hydrochloric and a drop or two of sulphurous acids, which mixture is then passed hot through the filter. A re-precipitation by ammonia is then made, and the precipitate collected again on the filter and added to the main one, the filtrate passing into the flask containing the previous one. If much manganese is present, of course a second precipitation by ammonia, of the small precipitate, may be required. In these cases there is no difficulty in getting all the manganese into the filtrate.

Treatment of the Alumina Precipitate.—The combined alumina, &c., precipitates are ignited moist, in the paper, unless considerable iron is present, when the main one is dried, removed as far as possible from the paper, and the latter ignited separately to prevent partial reduction of a portion of the iron, which can not then be re-oxidised by heating (see *ante*).

Alumina in the quantities ordinarily found can not be fully dehydrated by the full heat of the Bunsen burner. It must be blasted for five or ten minutes. If iron is present in large amount this last operation must be conducted so as to ensure free access of air to the crucible (see *ante*).

Estimation of Silica and Iron in the Alumina Precipitate.—The precipitate is dissolved by fusion with acid potassium sulphate, an operation which is accomplished without trouble in from two to four hours if the temperature is kept low, and the acid salt has been properly made free from water and excess of acid. The melt is taken up with hot water and considerable dilute sulphuric acid, the residue collected, weighed, and corrected by hydrofluoric and sulphuric acids for silica, which, as said before, rarely amounts to 1 milligrm. in weight, and further examined for barium (see *ante*) by dissolving in hot, strong sulphuric acid and diluting with cold water.* The filtrate is reduced, hot, by hydrogen sulphide, boiled to collect the sulphur and platinum sulphide resulting from the bisulphate fusion, the hydrogen sulphide being allowed to pass for a short time after boiling † It is then filtered‡ hot into a flask attached to a carbonic acid apparatus, and brought to boiling to expel hydrogen sulphide. When this is fully effected the flask is cooled in water while the carbon dioxide still passes, and the solution is then titrated by potassium permanganate. The results are strictly accurate when care is taken with the reduction by hydrogen sulphide, and the method is altogether superior to that of reduction by zinc, since no foreign impurity affecting the result is introduced, and the ever-present titanium is not also reduced. If this latter element has not already been tested for, its relative amount can be conveniently ascertained by adding hydrogen peroxide to the titrated ferric solution.

Alumina found by Difference.—In this laboratory titanium and phosphorus are estimated in separate portions, and likewise zirconium and chromium if present. The alumina is always found by difference after deducting their sum as oxides and the total iron as ferric oxide from the combined weights. This throws upon the alumina all errors involved in their separate determinations, but these may balance, and in any case the probable error can hardly be as high as that involved in the direct weighing of the alumina itself, considering the difficulty of effecting a satisfactory separation of it from all the

* The fact must not be overlooked that certain of the rare earths may pass completely into the filtrate if the basic acetate method is followed. If then, later on, rendering the combined filtrates ammonical, an unexpectedly large precipitate appears, this should be carefully examined as to its nature. In an analysis of piedmonite from Maryland over 2 per cent of rare earths, including cerium and others not identified, were quantitatively separated in this way from iron, alumina, &c.

† If, instead of sodium acetate, ammonia alone has been used to precipitate alumina, &c., it has sometimes happened in the experience of others than the writer that on concentration of the first filtrate a pale pale straw-coloured precipitate appeared which remained on the filter with the traces of alumina that may also separate, although it is slowly soluble in hot water. This is some compound of platinum, and attention is called to it here for the guidance of others who may notice it and be unaware of its character.

* Some years ago, in a series of analyses of rocks from the Leucite Hills, in Wyoming, there was obtained at this stage, when it was customary to dissolve the melt in cold water only preliminary to precipitation of titanium by boiling the neutralised sulphuric solution in presence of sulphur dioxide, a white, more or less flocculent residue amounting to 1 to 3 per cent of the rock, which was at first taken to be a mixture of tantalic and columbic acids. Eventually it was found to consist apparently of nothing but TiO_2 and P_2O_5, with perhaps a little ZrO_2. By repeated fusion with acid potassium sulphate and leaching with cold water it could be gradually brought into solution. It was these rocks which furnished the most striking instance of the peculiar, milky, sulphate residues previously mentioned as derived from the ignited silica. Knop (*Zeit. für Kyrst.*, vol. x., p. 73, 1885) seems to have obtained a similar mixture in analysing minerals from the Kaiserstuhl in Baden, but its nature was not ascertained, though suspected to be, if not silica, columbiferous titanic acid.

† It may be mentioned that the precipitation of platinum from a hot sulphate solution is far quicker and cleaner than from hydrochloric acid.

‡ Filtration is not necessary if only precipitated sulphur and no sulphides are in suspension, since this is without reducing action on cold permanganate solution, as Wells and Mitchell, and others before them, have pointed out. The above authors used this method of reducing ferric iron in titanic iron ores. (*Journ. Am. Chem. Soc.*, vol. xvii., p. 78, 1895; also CHEMICAL NEWS, vol. lxxiii., p. 123, 1896).

other admixtures, an operation which would, moreover, immoderately extend the time required for each analysis.

Alternative Method.—Should it be desirable for any reason to effect an actual further separation, this may best be done, up to a certain point, after the bisulphate fusion, by removal of the iron by ammonium sulphide in ammonium-tartrate solution, evaporation of the filtrate, ignition of the residue with sodium carbonate and nitrate, and extraction with water, whereby titanium and zirconium are left on the filter as sodium salts, and the chromium is carried into the filtrate as chromate. The further separation of Al_2O_3 and P_2O_5 from the chromium is outlined under the head of "Chromium." This is as far as the separation can well be carried, and the alumina must still be found by subtracting the P_2O_5 from the combined weights of the Al_2O_3 and P_2O_5. The possibility of loss of some P_2O_5 by volatilisation* during the bisulphate fusion must be borne in mind here, for if it takes place the final weight of Al_2O_3 and P_2O_5 will not contain all the P_2O_5.

Some writers recommend dissolving the ignited alumina, &c., in hydrochloric acid, but when the precipitate has been heated over the blast, as it should be, this is very ineffective.

(To be continued).

THE DETERMINATION OF SMALL QUANTITIES OF ALCOHOL.†

By FRANCIS G. BENEDICT and R. S. NORRIS.

(Concluded from p. 68).

In an experiment in which about nine-tenths grm. of 19 per cent alcohol evaporated in nine hours, no barium carbonate was formed. In two other experiments in which half that quantity of alcohol was used it was also completely absorbed by the sulphuric acid. Forty c.c. of concentrated sulphuric acid were used in each case.

Four solutions were prepared by this method, and the alcohol determined by titration. The results obtained were as follows:—

	Alcohol absorbed. M.grms.	Alcohol determined. M.grms.
I.	96·77	95·05
II.	90·87	89·66
III.	41·62	41·50
IV.	13·5	14·4

Two experiments were made to determine how much alcohol a given volume of concentrated sulphuric acid can completely remove from a current of air. In the U-tube immediately preceding the acid 90 per cent alcohol was placed, and its evaporation was facilitated by a loose roll of filter-paper in the limb of the tube next to the acid. Air was drawn through this apparatus for fifteen hours at the usual rate before a distinct appearance of barium carbonate precipitate occurred. The coating of the carbonate on the sides of the barium hydroxide tube was, at the end of this period, less in amount than that produced by the combustion of a milligrm. of alcohol. During the period approximately 40 c.c. of alcohol was evaporated. The sulphuric acid solution measured about 90 c.c., and had a brownish red colour and a faint pleasant ethereal odour. It was made up to 100 c.c. with concentrated sulphuric acid, and five-tenths c.c. measured out and made up to 50 c.c. with more acid. This solution was titrated with the chromic acid solution and found to contain 3·43 m.grms. of alcohol in each c.c. Accordingly the 50 c.c. of concentrated sulphuric acid used in the first experiment had absorbed 34·3 grms. of alcohol.

In the second experiment only 30 c.c. of sulphuric acid were used, and the alcohol was made to evaporate more rapidly. About 20 c.c. of 90 per cent alcohol were volatilised in eight hours. In the beginning of the experiment the rapid absorption of the alcohol by the sulphuric acid caused an appreciable rise in the temperature. The sulphuric acid solution was diluted as in the first experiment, and the alcohol determined to be 1·72 m.grms. in each c.c. The 30 c.c. of sulphuric acid had therefore absorbed 17·2 grms. of alcohol.

For the determinations of alcohol in dilute solutions we have found the following method the most satisfactory. Having prepared the standard solutions above described and determined the value of each in terms of the others, the strength of the unknown solution of alcohol is first determined roughly by means of an ordinary pycnometer.

If the solution contains more than 1 per cent of alcohol, weigh out accurately such a quantity as will contain about one-tenth grm. of absolute alcohol into a 50 c.c. graduated flask, add 10 c.c. concentrated sulphuric acid carefully, the flask being immersed in cold water and continuously shaken to prevent a rise in temperature. The solution is then made up to the 50 c.c. mark with concentrated sulphuric acid, thoroughly mixed, transferred to a burette, and about 5 c.c. drawn off into a small flask. Twenty c.c. of the chromic acid solution are then added, using the same precautions for the delivery of the solution as when it was standardised. The contents of the flask are heated to 98° C. (a thermometer being immersed in the liquid) and kept at this temperature for five minutes. The solution is then cooled down to the room temperature, poured into 200 c.c. of distilled water, and ferrous ammonium sulphate added from a burette until the excess of chromic acid is completely reduced, as is indicated by the disappearance of the red colour. The excess of ferrous ammonium sulphate is then determined with the standard potassium permanganate. It is best to add a single drop of the potassium permanganate solution at first in order to be sure that there is an excess of ferrous ammonium sulphate present. The amount of alcohol per c.c. is calculated thus:—The amount of ferrous ammonium sulphate solution used (after making allowance for the permanganate required for the back titration) is subtracted from the number of c.c. of ferrous ammonium sulphate equivalent to the chromic acid solution used, and the result divided by the number of c.c. of the alcohol solution taken. This gives the volume of ferrous ammonium sulphate solution in c.c. equivalent in reducing power to 1 c.c. of the solution of alcohol. Multiplying this by the factor previously determined, which expresses the number of m.grms. of alcohol equivalent to one c.c. of ferrous ammonium sulphate, gives the weight of alcohol in 1 c.c. of the sulphuric acid solution.

If the original solution contains 1 per cent or less of alcohol, draw 0·5 c.c. into a 100 c.c. flask, and add about 5 c.c. of concentrated sulphuric acid, keeping the liquid cool during the addition. Add 10 c.c. of the chromic acid solution and proceed as above. This determination will serve to indicate approximately how much alcohol there is in the solution, so that in subsequent titrations enough of it can be taken to reduce from 60 to 80 per cent of the chromic acid. The amount of sulphuric acid added in each case should be equal to about twice the volume of the solution of alcohol used.

* G. Rose speaks of such loss when volatilising sulphuric acid in presence of phosphoric acid. "Handb. f. Quant. Anal.," Finkener edition, vol., ii., p. 575, and elsewhere.

† From the *Journal of the American Chemical Society*, xx., No 4.

OBITUARY.

Mr. J. A. R. NEWLANDS, F.C.S., F.I.C.

It is with much regret that we record the death of Mr. J. A. R. Newlands, who passed away on the 29th of July, at his residence at Lower Clapton, N.E., aged 60.

Mr. Newlands was best known among scientific chemists as being the first to point out the periodic relations between the atomic weight of the elements, for

which perhaps too much credit has been given to M. Mendeleeff. This new law, provisionally called the "Law of Octaves," was first mooted in the CHEMICAL NEWS in vol. vii., p. 70, February 7, 1863. In another paper in July, 1864, a list of all the known elements was given both in order of their atomic weights and in a table giving a horizontal arrangement of the more important elements, also in order of atomic weight, with blanks corresponding to some of the missing members of the various groups. Thus, in the trivalent group, commencing with boron, there was a blank next below zinc, since filled by gallium, and another below cadmium now filled by indium. On August, 20th 1864, Mr. Newlands announced the existence of a simple relation between the elements when thus arranged, to the effect that the eighth element, starting from any given one, was a sort of repetition of the first. Some years afterwards the brilliant work of Sir H. Roscoe showed the atomic weight of vanadium was 51·2 instead of 137. This reduction at once placed vanadium in the same line as the phosphorus group, thereby confirming the periodic law. Mr. Newlands leaves a large circle of friends, by whom his genial companionship will assuredly be missed. In the year 1887 Mr. Newlands was awarded the Davy Medal of the Royal Society, in recognition of his work on the Periodic Law of Elements.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxx., January 24, 1898.

Gravimetric and Volumetric Estimation of Hydroxylamines and of Hydrazine.—K. A. Hofmann and F. Kuspert.—The authors estimate hydroxylamine and hydrazine by oxidising them by means of a dilute solution of sulphate of vanadyl, measuring the nitrogen give off, and titrating the sulphate of vanadium formed by $KMnO_4$.

$$2NH_2OH + O = N_2 + 3H_2O,$$
$$N_2H_4 + 2O = N_2 + 2H_2O.$$

The whole of the nitrogen is set free at 60° in a few minutes. The solution of the vanadyl salt is obtained by dissolving the metavanadate of ammonium, $VdO_3.NH_4$, in concentrated sulphuric acid, and then diluting. The material to be analysed is dissolved in dilute sulphuric acid, and the vanadic solution added until it takes a green colouration; it is then heated to 60°, the nitrogen measured, &c. The end of the titration is shown by the appearance of a pale yellowish-rose tint.

Some Syntheses effected with Chlorofumaric Ether.—W. Beckh.—By treating a solution of ethenyltricarbonic ether in absolute alcohol by C_2H_5ONa and chlorofumaric ether, we obtain principally butylenepentacarbonic ether—

$$C_2H_5CO_2CH_2C=(CO_2C_2H_5)_2$$
$$C_2H_5CO_2CH=C - CO_2C_2H_5,$$

in the form of a viscous liquid insoluble in acids, alkalies, and water; it boils at 229—231° (13 m.m.). By saponifying this ether by $Ba(OH)_2$, we obtain butylene-tetracarbonic acid, fusing at 175—176°, easily soluble in water. The salts of silver and lead give white precipitates. At the same time as the formation of the ether, oily products are formed, giving a red colouration with $FeCl_3$; they will not distil without decomposition. Amylenepentacarbonic ether has been prepared by acting with chlorofumaric ether on carboxyglutarate of ethyl in the presence of C_2H_5ONa. It is a yellow liquid, boiling at 240—250° (15 m.m.), condensing under the influence of C_2H_5ONa at 120°, giving a cyclic compound—

$$CH(CO_2C_2H_5) - CO$$
$$CH_2 \qquad\qquad CH$$
$$C(CO_2C_2H_5)^2 - C.CO_2C_2H_5$$

which is coloured indigo-blue with $FeCl_3$.

Methylation of Hydrate of Hydrazine.—C. Harries and T. Haga.—By treating hydrate of hydrazine with increasing quantities of CH_3I we obtain successively methyl-hydrazine, dissymmetric dimethyl- and trimethyl-hydrazine. The iodhydrate, $NH_2NH(CH_3)_2I$, crystallises in water in flakes; it is fusible at 235° with decomposition, and soluble in ethylic and amylic alcohols. The chlorhydrate is hygroscopic. The oxalate of dissymmetric dimethyl-hydrazine, $(CH_3)_2N.NH_2(CO_2H)_2$, crystallises in alcohol in plates, fusible at 143° and insoluble in ether. By treating methyl-hydrazine (3 molecules) by 2 molecules of benzoic aldehyd in aqueous solution, we obtain tribenzylidene-methylhydrazine in the form of white needles, fusible at 109°, soluble in alcohol and ether, but insoluble in water.

Splitting-up of Sylvane into Levulic Aldehyd (Pentanone 3 to 1·1); Researches on the Constituents of Beech Tar.—C. Harries.—Sylvane (α-methylfurfurane) is contained in considerable proportions in beech tar, in the portion boiling between 60° and 70°. This portion is exhausted by bisulphite at 40 per cent, and then by NaHO at 10 per cent. The residue dried over K_2CO_3 gives a liquid boiling at 60° to 70°. This is heated with sodium on the water-bath until there is no further reaction, and on fractionating almost pure sylvane is obtained, boiling at 65° with a density at 18° of 0·827. When heated at 120° with dilute hydrochloric acid, we obtain levulic aldehyd and its products of condensation. Methylal is easily obtained by heating 500 grms. of sylvane dissolved in 1500 c.c. of methylic alcohol, with 20 parts of methylic alcohol containing 80 per cent of hydrochloric acid gas, for twenty-four hours in a flask fitted with a vertical condenser. After precipitating with water it is dried and fractionated *in vacuo*. Methylal boils at 87—88° (17 m.m.), and has a density of 0·9684 at 18°. It is slightly soluble in water, and easily so in organic solvents. Acetal is obtained in an analogous manner, and boils at 93° (12 m.m.); it is a colourless liquid, with an agreeable odour, and slightly soluble in water. By heating methylal for ten minutes with dilute hydrochloric acid, and then neutralising with $NaHCO_3$, and then with K_2CO_3 in the presence of ether, we obtain levulic aldehyd in the form of a liquid boiling at 70° (12 m.m.), and at 108° at the normal pressure, having a density of 1·0156 at 16°. It is soluble in all proportions in water and in the organic solvents. It is stable when pure, but under the action of acids and alkalies it polymerises with great ease. Moist Ag_2O transforms it rapidly when warmed into levulic acid.

Recent Progress in Lighting by means of Flame.—H. Bunte.—The author shows that oxide of cerium is the only luminous excitant in the Auer mantle; its *role* is explained as follows:—The cerium, equally disseminated over a skeleton of thorina, provokes the rapid combination of H_2+O (as does platinum sponge), and being the only material to profit by the heat given off by the reaction, on account of the bad conductivity and the low specific heat of the thorina, the ceric oxide is carried to a temperature sufficiently high to make it strongly luminous.

Justus Liebig's Annalen der Chemie,
Vol. ccxcvii., Nov. 23, 1897.

Research on the Substituted Succinic Acids.—K. Auwers.—In this note the author gives a *résumé* of the results he has obtained with different collaborators. Of the twenty-four possible acids, $C_7H_{12}O_4$ still wants those of the *tertiary malonic butyl*, and the two stereo-isomers *αβ-dimethylglutaric*. He thinks that the αβ-dimethyl-

glutaric acid recently described by Montemartin is only a mixture of the two stereo-isomers. The fact that symmetric di-isopropylsuccinic acid has only one modification is perhaps due to the accumulation of the groups CH_3, and not to the complication of the molecule.

Symmetric Methylethylsuccinic Acids.—K. Auwers and R. Fritzweiler.—These acids were prepared by the action of a bromobutyric ether on the soda methylmalonate of ethyl at 160°—180°. The ether of the tricarbonated acid thus obtained distils at 158°—161° (16 m.m.), and after saponification with sulphuric ether the two symmetric methylethylsuccinic acids which are separated by crystallisation; fumaroidic acid first crystallises, but in long needles, while the mother-liquor contains principally malenoidic acid, which is more fusible than the glutaric derivatives. The author then describes the preparation and properties of a large number of derivatives.

On Asymmetric Methylethylsuccinic Acid. — K. Auwers and R. Fritzweiler.—This acid was obtained by the action of malonic soda ether on methylethylacetic ether. To prepare this latter the authors first prepared ethylmalonic ether; then ethylmethylmalonic ether, by the successive ethylation and methylation of malonic ether, and then saponifying the ether and heating the ethylmethylmalonic acid to get rid of the CO_2. The ethylmethylacetic acid was then bromised and etherified. The action of malonic soda ether on this body, to obtain the tricarbonated ether, gives but a poor return (29 per cent). The methylethylsuccinic acid passes over at 145°—155° (30 m.m.), and the glutaric derivative at 190°—210° (30 m.m.).

The Isopropylsuccinic Acid Derivatives of Amylene. — K. Auwers and F. Meyer. — The amylene boiling at 29°—35° was converted into dicyanide, and the acid resulting from the saponification of this nitrite was recognised as *isopropylsuccinic acid*.

The Symmetric Bidecylsuccinic Acids.—K. Auwers and F. Betteridge.—Lauric acid, $C_{10}H_{21}.CH_2.CO_2H$, was bromised and then etherified. The α-bromolaurate of ethyl distils at 170°—174° (11 m.m.). From this bromised ether bidecylsuccinic ether is prepared, distilling at 200°—205° (12 m.m.).

On δ-Methyluric Acid.—W. von Lœben.—Not suitable for abstraction.

On Phenacetylmalonic Ether.—H. Metzner.—This ether, prepared by chloride of phenylacetyl and malonic soda ether, gives benzylmethylacetone,—

$$C_6H_5.CH_2—CO.CH_3,$$

when warmed with HCl. Soda splits it up into malonic ether and phenyl-acetic acid. An analogous splitting-up is produced by concentrated NH_3, which gives malonic and phenacetic amides.

MISCELLANEOUS.

Sulphate of Ammonia Committee Prize Essay.—We may draw attention to the offer by the Sulphate of Ammonia Committee of the sum of 500 guineas for the best essay on "The Utility of Sulphate of Ammonia in Agriculture." The subject is to be treated from a practical and scientific point of view. The committee, we are told, has secured the services of Mr. William C. Little and Dr. Voelcker to act as judges of the essays, and in the event of any difference arising, Mr. Samuel Rowlandson will act as referee. The essays must be in the English language, and be in the hands of the Chairman of the Committee not later than November 15. The selected essay will become the property of the committee, who reserve to themselves the right to make such use of it as they may think fit. The committee also reserves to itself the right to purchase for a sum not exceeding 50 guineas any of the other essays. Further particulars can be obtained of Mr. W. G. Blagden, Chairman of the Sulphate of Ammonia Committee, 4, Fenchurch Avenue, London, E.C., to whom we would refer intending competitors.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1898, the Laboratory was attended by 38 students. These may be divided, according to their respective countries, as follows: — From the German Empire there were 26; from Austria, 3; from England and from Brazil, 2; from Luxemburg, Russia, and Bulgaria, 1 each. There were 3 Assistants in the Instruction Laboratory, and 23 in the Versuchsstationen (private laboratories). In the certified body of Teachers there has been no change: to this body belong the Directors, Professor Dr. H. Fresenius, Professor Dr. W. Fresenius, Professor Dr. E. Hintz, and also Dr. med. G. Frank, Dr. W. Leng, Dr. L. Grünhut, and T. Brahm (architect). On the 25th and 26th May, 1898, the Laboratory was able to celebrate the event of its fifty years' existence. The continuation of support from the State has been guaranteed to the Institution, together with the right of the practical instruction of provision and food analysts for the final examination. The Winter Term begins on October 17th. Besides scientific work, numerous researches have been made during the past Summer Term in the interest of commerce, industry, mining, agriculture, sanitation, law, and the administration, in the Versuchsstationen (private laboratory).

Methyluric Acid and Dimethyluric-1.7-Acid. — E. Fischer and H. Clemm.—Methyluric acid is easily prepared from theobromine, which is oxidised by HCl and $KClO_3$ and precipitated with SH_2; this gives dimethylalloxantine, which is treated with HNO_3 and transformed into methylalloxane. One part of methylalloxane is heated with 12 parts of a concentrated solution of sulphide of ammonium at 80° for six hours. After cooling, the precipitate is transformed into methyluranile by HCl gas. This body is warmed with one part of CNOK and three parts of water until the red colour disappears. On cooling, methylpseudourate of potassium crystallises out; this is decomposed with HCl. The methyl-pseudo-uric acid is transformed into methyluric acid by heating with 9 parts of HCl at 20 per cent for one hour on the water-bath. Methyluric acid, $C_6H_6N_4O_3$, crystallises in needles decomposing without melting at 400°. Dimethyluric acid-1.7 is prepared by heating three parts of methylalloxane with five parts of methylamine at 33 per cent, previously saturated with SO_2. The cooled solution is treated with excess of HCl. The dimethyl-pseudo-uric acid obtained is heated with KCl at 20 per cent, which gives dimethyluric acid-1.7.—*Ber. Deutsch. Chem. Gesell.*

HERIOT-WATT COLLEGE, EDINBURGH.

F. GRANT OGILVIE, M.A., B.Sc., F.R.S.E., Principal.

DAY CLASSES—SESSION 1898-99.

The SESSION extends from TUESDAY, October 4th, 1898, to Friday, June 2nd, 1899.

These classes provide Courses of Study extending over one or more years, suitable for Students who have previously passed through the Curriculum of a Secondary School. The principal Courses are:—Physical and Chemical, Mechanical Engineering and Electrical Engineering. There are also classes in French, German, Drawing, and Practice of Commerce. Class Fees from £1 1s. to £4 4s.; Session Fee, £10 10s.

There is also a preparatory Course of Instruction for Agricultural Students; Session Fee, £5 5s. An extract from the Calendar of the College giving particulars of the Day Classes, and of the various Appliances, Laboratories, and Workshops available for instruction, may be had on application to the Librarian, at the College, or to the Treasurer of George Heriot's Trust.

DAVID LEWIS,
Treasurer.

Treasurer's Chambers, 20, York Place,
Edinburgh, July 18th, 1898.

THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2021.

ON BLUE GLASSES WITH A BASE OF CHROMIUM.

By ANDRE DUBOIN,
Professeur adjoint à la Faculté des Sciences de Clermont-Ferrand.

THE experiments through which sapphire has been reproduced have led people to think that the fine blue colour of that gem is due to chromium. Ste.-Claire Deville and Caron (*Comptes Rendus*, 1858, xlvi., p. 764), after their experiments on the reproduction of corundum, in the course of which they obtained both sapphire and ruby, are quite positive on this point. "Blue sapphire," they say, "is produced under the same circumstances as ruby. It is likewise coloured by oxide of chromium. The only difference between them lies in the proportions of the colouring matter, perhaps also in the state of oxidation of the chromium. But analysis can give no accurate results on this point, owing to the very small quantity of colouring matter present in all cases. In certain preparations people have obtained, side by side, red rubies and sapphires of the finest blue, whose tint is, moreover, exactly the same as that of the Oriental sapphire, the cause of which is unknown."

Later on, Gaudin (*Comptes Rendus*, 1869, xlix., p. 1343) observed that the oxide of chromium, heated in the reducing flame of the oxyhydrogen blowpipe, takes a sky-blue tint, though somewhat greenish. This tint is to be found in some Ceylon sapphires.

The blue tint of sapphire is due to chromium, so it must be possible to obtain, with the help of the compounds of chromium, blue glasses by operating in a reducing medium.

I at first ascertained that, by heating some alumina along with a small quantity of oxide of chromium, a pink colour is always obtained; but I have obtained no blue colour by heating it along with a reducer (charcoal, aluminium, &c.).

In such cases oxide of chromium was entirely reduced. Oxide of chromium, highly heated with aluminium in small particles, is reduced with explosion.

Then I operated with B_2O_3 and SiO_2 with a view to obtaining glasses.

At first I tried the hard glasses, with a base of alumina, used in the making of artificial gems.

It is known that with this object fusible mixtures are used, the composition of which comes very near the formula $4{\cdot}5SiO_2,Al_2O_3,3CaO$. Part of the lime may be replaced by an equivalent quantity of baryta to obtain glasses having more brilliancy, and whose density comes nearer to that of precious stones.

With a view to colouring these glasses by means of the oxide of chromium I proceeded as follows:—I heated to vivid redness for five hours, in a crucible brasqued with charcoal, the vitrifiable mixtures with some neutral chromate of potash. I have, moreover, ascertained that this salt may be replaced by an equivalent quantity of $Cr_2O_7K_4$ or Cr_2O_3.

1. A mixture of SiO_2 (135 parts), Al_2O_3 (51), CO_3Ca (150), CrO_4K_2 (9), to which some arseniate of potash has been added, gives a crystalline mass which I mean to study at greater length, but which, from our present point of view, has only a somewhat dull blue tint.

2. On the contrary, compounds which contain baryta give most beautiful blue glasses. I replaced the whole quantity of lime by the equivalent quantity of baryta. The vitrifiable mixture used is made up of SiO_2 (135 parts), Al_2O_3 (51), CO_3Ba (295·5), CrO_4K_2 (7). It gives when melted a very fine blue glass.

I was then led to seek whether I could not obtain a composition still more fusible and equally bright. It is known that a mixture of CO_3K_2 and CO_3Na_2, or KCl and NaCl, or K and Na, melts at a lower temperature than each of the bodies taken separately.

I therefore tried to replace half the lime by the equivalent quantity of baryta; the mixture used being composed as follows:—SiO_2 (135 parts), Al_2O_3 (51), CO_3Ba (148), CO_3Ca (75), CrO_4K_2 (9). It gives, when melted, a very fine blue glass.

3. *Glasses with Boric Acid.*—It is known that in glasses a part of the SiO_2 may be replaced by boric acid. I obtained a glass of a very fine blue tint, but too easily attacked by acids, by melting under the same conditions as before a mixture of B_2O_3 (4 parts), Al_2O_3 (1 part), CrO_4K_2 (1 part). In this experiment a glass is obtained which is surrounded with a pellicle of metallic chromium. Very often the crucibles are pierced. If borax is substituted for boric acid, the alumina is reduced. In an experiment in which I had heated a mixture of borax and alumina with a small quantity of CrO_4K_2 and a quantity of SiO_2 equal to two-fifths of the alumina, a metallic pellicle was formed, consisting for the most part of aluminium.

I made numerous experiments until I found the composition of a glass made by Messrs. Schott and Co. at Jena. I have been able to colour this glass blue by means of the oxide of chromium. The mixture used was composed as follows:—SiO_2 (84 parts), Bo_2O_3 (39), Al_2O_3 (16), CO_3Ba (157·6), CrO_4K_2 (7).

In the course of my numerous experiments on this subject, I tried various reducers; among others, Al and carbide of calcium. Aluminium did not lead to good results; but, by operating at a higher temperature, it might be possible to obtain results more satisfactory than those I obtained. As for C_2Ca, it gave me blue glasses, not so fine, however, as the above-mentioned. In the latter case I operated in a graphite crucible. Practically, there would be some difficulty in regulating the quantity of C_2Ca to be used, as the material employed is always somewhat hygroscopic.

4. *Common Glasses.*—Common glasses, or the mixtures used in obtaining them by melting, did not give good results. A mixture of 100 parts of quartz, 30 of CO_3K_2, 15 of CO_3Ca—a composition answering to that of Bohemian glass—to which 7 parts of CrO_4K_2 are added, gives a glass which has a bluish violet hue only in the vicinity of the layer of carbon. Better results might perhaps be obtained by heating during a longer time. As for glass itself, pulverised and melted with CrO_4K_2, it gave me only a green glass.

ON THE ANALYSIS OF CRUDE TARTROUS MATERIAL.

By M. J. SCHAFER.

AMONG the many methods for the estimation of tartaric acid in tartrous substances, the one most used is that of Goldenberg—a process which is based on the setting free of the tartaric acid by means of hydrochloric. The free acid is transformed into a neutral potassic salt by means of carbonate of potassium. The liquid is evaporated down to a small volume (10 c.c.), and glacial acetic acid is added; this causes the partial precipitation of the tartar. To make the precipitation complete we add a known volume of alcohol at 96 per cent, allow to stand for a certain time, then filter. The precipitate is washed, dissolved in warm water, and the solution thus obtained titrated while still warm with normal soda.

Such is, in brief, the original process which has been adopted in most laboratories. However, with this process

a larger proportion of tartaric acid is found than is really present in the substance examined, and this error—though relatively small—is considerably augmented if the original method is not closely followed. It is in this manner that Möslinger introduced certain modifications giving wide variations. For observing the progress of the titration this author used azolithmine with a violet shade instead of red litmus-paper; he left the precipitate formed by the glacial acetic acid for a whole night in the aceto-alcoholic liquor, while by Goldenberg's method only a short time of standing is recommended; to precipitate the tartar he used 5 c.c. of glacial acetic acid, while the original process only speaks of 2 to 2·5 c.c.

By using blue azolithmine paper the titration is continued until a drop of the liquid placed on the paper no longer produces a red colouration, while in the original process it is stopped when a drop gives a slight blue colour to red litmus-paper. In the case of mineral acids there is no difference between these two indicators, but it is altogether different with tartaric acid; in this case the change from red to blue is retarded. This applies even to chemically pure tartar. But when we have to deal with crude tartars or wine lees, still other factors intervene and increase the difficulties of the titration. The precipitate caused by the glacial acetic acid contains, besides the tartar and chloride of potassium, other bodies which neutralise a certain quantity of the alkaline solution, and thus cause a doubtful reaction. It is for this reason that it often happens that the red litmus-paper becomes decidedly blue, while the azolithmine paper is still red. The difference that these two critical points will sometimes reach is as much as 1·5 to 2 per cent, especially with poor samples.

The time during which the precipitate caused by the glacial acetic acid is left standing also has a considerable influence on the results of the analysis. I have proved that the precipitation is complete at the end of a quarter of an hour, and that by letting the solution stand too long the results obtained are too high, on account of the formation of a flocculent precipitate which saturates a certain quantity of the alkaline solution. Below we give some very interesting results:—

	Tartaric acid found after standing for—		
	¼ hour.	3 hours.	12 hours.
French lees ..	23·24	23·47	24·27
Spanish lees ..	24·93	25·17	26·16
Portuguese lees..	24·22	24·67	25·29
Unknown lees ..	15·45	15·67	16·27
Portuguese tartar	54·22	54·64	54·94
Portuguese lees..	22·80	23·00	23·50
Spanish lees ..	28·27	28·68	29·36
French lees ..	27·88	28·17	28·66
Algerian lees ..	21·87	22·57	22·87

But by exhausting the material by a mixture of ether and alcohol before analysing, the precipitate can be left for a considerable time without the results being adversely affected. Below will be found some figures on this subject:—

	Tartaric acid found—	
	Filtering immediately.	After 12 hours.
Italian lees ..	29·33	27·38
Spanish lees ..	25·27	25·37
Spanish lees ..	28·60	28·70
Algerian lees ..	22·33	22·33

These small differences are due to the inevitable errors of observation. My researches have enabled me to arrive at the following conclusions:—

1. The end of the titration should be decided by the use of pale red litmus-paper.

2. The operation is complete when a drop of the liquid placed on this paper forms a circle bordered with blue.

3. As soon as the glacial acetic acid has completed the precipitation of the tartar, the liquid should be filtered,—if not, another body is formed which saturates a certain quantity of the alkaline liquor, and thus causes too high a result. The quantity of this body formed is in direct proportion with the time the solution is left standing.

4. When the material is exhausted with a mixture of ether and alcohol, before analysis, the whole may be allowed to stand for a much longer time without inconvenience.—*Chemiker Zeitung*, 1898, p. 255.

ON ANHYDROUS AND CRYSTALLISED SULPHIDE OF MAGNESIUM.

By A. MOURLOT.

SULPHUR and magnesium unite directly at about 600°, forming a sulphide with the formula MgS, which is recognised as a grey, porous, amorphous, and infusible mass. A certain number of reactions enable us to obtain this compound indirectly; in the latter case we obtain a white powder which decomposes very readily.

The research we have made on the action of a high temperature, and of reducing agents on sulphates, made it possible for us to obtain this body melted and crystallised.

I. *Preparation of the Amorphous Sulphide.*—It was necessary for the proper carrying out of these researches to be able to prepare fairly large quantities of the amorphous sulphide: for this purpose, after having tried either Fremy's method (*action of sulphide of carbon on magnesia at a red heat*), or that of Reichel or of Parkinson (*action of sulphur vapours carried by hydrogen over red-hot magnesium*), we finally adopted the two following methods:—

1. We placed a mixture of magnesium filings and a small quantity of sulphur in a carbon boat, which was placed in a porcelain tube heated in a reverberatory coke furnace; the tube was traversed by a continuous current of sulphuretted hydrogen; the reaction takes place with strong incandescence. We thus obtain rapidly the amorphous sulphite of a white colour, or with a slight greyish tinge.

2. A second process consists in making sulphuretted hydrogen react on the anhydrous sulphate, or on pure magnesia heated to about 1200°; however, the complete transformation of the magnesia into sulphide is very slow, as shown by Reichel (*J. f. Prakt. Chim.*, xii., p. 55). If we operate on 20 grms. of sulphate the transformation is complete after four or five hours' heating; abundant sulphur vapours are given off, as well as sulphurous acid gas and water.

In these two methods we use an apparatus for the continuous supply of sulphuretted hydrogen. The tube is allowed to cool in a vapour of hydrogen.

On analysing the amorphous sulphide we obtained the following results:—

	I.	II.	Theory.
Mg ..	43·05	43·15	42·85
S ..	56·85	56·80	57·15

II. *Preparation of the Melted and Crystallised Sulphide.*—1. The amorphous sulphide is placed in a carbon boat, and the latter is introduced into the carbon tube of a tubular electric furnace. After about six minutes heating by means of a current of 1000 ampères and 50 volts, we obtained a globular yellowish mass, of a brilliant appearance and well melted: this experiment was repeated a certain number of times, varying the time of heating, but we always obtained the same product.

2. We further tried to prepare the crystallised sulphide directly, in the electric furnace, by reducing the anhydrous sulphate by carbon. This method, which gave us such good results with the alkaline earthy sulphides, only gave in this case an incomplete transformation of

the sulphate into sulphide, a certain quantity of the sulphate being at the same time brought to the state of magnesic oxide.

3. We then endeavoured to utilise the phenomena of double decomposition which might take place between the chloride of magnesium and certain sulphides. For this purpose we mixed sulphide of magnesium, in slight excess, with proto-sulphide of tin, in the proportions shown by the formula $MgCl_2+SnS$, and we submitted this mixture to the action of a current of 1000 ampères and 50 volts. There was an abundant disengagement of vapours of chloride of tin, and after about seven or eight minutes the heat was stopped, and small globules of melted sulphide of magnesium were found, completely identical with that produced by the fusion of the amorphous sulphide. The analysis of the crystallised sulphide gave us:—

	I.	II.	Theory.
Mg ..	43·23	43·6	42·85
S ..	56·65	56·3	57·15

Properties.—Melted sulphide of magnesium is formed of large globules with a crystalline fracture often showing faces of cubical crystals; two distinct cleavage planes have been observed at right angles to each other; these crystals do not act upon polarised light; they are insoluble and are without action on essence of turpentine at the ordinary temperature; their density, taken in this liquid, is 1·85.

Hydrogen is without action on crystallised sulphide of magnesium at the highest temperature which can be obtained in a reverberatory furnace. Chlorine reacts at about 300°, with incandescence, producing anhydrous chloride of magnesium as well as chloride of sulphur. Bromine and iodine react at a dull red heat with the formation of the corresponding bromides and iodides, but without incandescence.

The action of oxygen is also very vigorous, and takes place with a slight elevation of temperature, though without any disengagement of sulphurous acid gas. The energetic oxidising agents, chlorate of potassium, binoxide of lead, and nitrate of potash, all react with incandescence.

With phosphoric anhydride there is further the production of a sulphide of phosphorus.

Phosphorus does not react on crystallised sulphide of magnesium; the experiment was tried in a current of carbonic acid gas, and there was no trace of any reduction even at 1000°. Boron and silicon, heated with the sulphide in a current of hydrogen, do not react up to a red-heat. The action of carbon was tried in the electric furnace; after heating for about fifteen minutes with a current of 1000 ampères and 50 volts, no reduction took place.

Iron is without action at a dull red-heat; sodium, on the contrary, does react, but without incandescence.

Aqueous vapour reacts directly with the production of magnesia and the disengagement of sulphuretted hydrogen; at the ordinary temperature the crystallised sulphide is very difficultly attacked by water, though in the case of the amorphous sulphide the decomposition is immediate. Concentrated nitric acid attacks it in the cold with the formation of sulphur; sulphuric acid, even when diluted, reacts at the ordinary temperature with the disengagement of sulphuretted hydrogen.

Gaseous hydrofluoric acid as well as hydrochloric acid gas react in the cold; by slightly heating, incandescence takes place with the production of the anhydrous fluoride or chloride. The reaction with hydrobromic and hydriodic acids take place at a dull red-heat with the formation of the bromide or iodide; but in this case there is never any incandescence.

The metallic chlorides react on crystallised sulphide of magnesium, under the influence of a slight rise of temperature; with the trichloride of phosphorus the reaction takes place with a considerable disengagement of heat and the formation of sulphide of phosphorus.

With subchloride of chromium the reaction is also very vigorous; in this latter case a greenish body containing chromium and sulphur is produced. We shall follow up the study of this body.

To sum up:—1. We have described an easy method for the preparation of anhydrous sulphide of magnesium. 2. We have prepared crystallised sulphide of magnesium both by the fusion of the amorphous sulphide and by the action of chloride of tin on anhydrous chloride of magnesium. 3. From the study of the properties of crystallised sulphide of magnesium we find that this sulphide is much less easily decomposed than the amorphous sulphide, and that it resembles sulphide of barium in most of its reactions. It is particularly remarkable for its complete irreducibility by carbon, which ranges it with the sulphides stable at a high temperature.—*Comptes Rendus*, cxxvii., No. 3.

THE

INVERSION OF SACCHAROSE BY WATER.

By MM. RAYMAN and SULE.

The mechanism of the inversion of saccharose has up to the present remained very obscure. The acids capable of producing the inversion have not the property of forming any combination with either of the two sugars resulting from the hydrolysis of the molecule; and, admitting that such compounds are formed, they should be very unstable and instantly destroyed by water; in fact a grouping—

$$\begin{matrix} -OH \\ -C-OCl \\ -H \end{matrix} \quad \text{or} \quad CH\!<\!\begin{matrix} OH \\ O-NO_2 \end{matrix}$$

would be very easily attacked by water. In the case of organic acids, we could easily imagine the production of relatively stable acid-aldehyds, but this hypothesis cannot be correct, as a very small quantity of acid suffices to hydrolyse a large quantity of sugar. On the other hand, we are well aware that the inversion by water only is possible above 110°. When we mix an acid with the water, the minimal temperature of inversion is lowered in proportion as the acid is energetic, and the inversion by water in the presence of acids may be considered as a generalisation of the laws established by Landolt and Ostwald.

There is already abundant but contradictory literature on the subject of inversion by water. Monier and Trevor found that a neutral aqueous solution could be kept at a temperature of 100° to 105° for two hours and a half without undergoing decomposition. Soubeyran gives polarisations of such an irregular character that they really cannot be believed.

In our experiments we took very great care to use only the very purest saccharose, and water completely free from any foreign matter. The water was distilled in a Bohemian glass retort after permanganate of potash had been added to it, and the distillate was again distilled with alum. Its electric conductivity, after this treatment was 1×10^6.

To prepare the saccharose we dissolved 250 grms. of the refined material, as pure as we could obtain it, in 150 grms. of warm water; the syrup was filtered through cotton-wool, and after cooling was poured in a very fine stream into one litre of alcohol at 96 per cent while constantly agitating. The following day there was a crust of crystals of saccharose on the surface. The mother-liquor was decanted, the crust washed with alcohol, and a fresh solution of 250 grms. of sugar in 150 grms. of water was added. This treatment was repeated three times; these crystalline crusts were coarsely powdered, washed first in alcohol, then in ether, and dried in vacuo at 40°—45°.

The rotatory power of the sugar thus obtained is $a_D = +66{\cdot}55$.

Decomposition of Saccharose by Water in Glass Vessels.—We made a number of solutions of different concentrations in both Bohemian and Jena glass vessels; these were boiled and the glasses weighed both before and afterwards. Solution No. IV. was heated on a water-bath; the polarisations obtained in a tube 10 centimetres long were :—

Time.	I.	II.	III.	IV.
0 hour	3·22	6·01	11·66	11·66
6 hours	3·24	6·10	11·66	11·67
67 ,,	3·24	5·96	11·57	11·64
33·5 ,,	3·24	—	10·56	10·97
61 ,,	3·14	—	5·94	6·82

Thus the inversion is the more complete as the solution is the more concentrated; the boiling-point is only 0·8° higher than that of water. The results are not varied by passing a current of oxygen through the boiling solution, and the solutions remain perfectly neutral.

We may therefore admit that even a prolonged boiling will not invert weak solutions.

The presence of the smallest quantity of salts, indicated by an increase of conductivity, increases the inversion. Thus a 20 per cent solution of saccharose made with a water whose conductivity was 20×10^6 gave as polarisation :—

Hours . ..	0	4	8	12	16	20	24
Polarisation	11·8°	11·67°	11·34°	9·74°	5·26°	0·23°	2·53°

Decomposition by Water in Platinum Vessels.—We used a platinum flask with a condenser of the same metal. After having kept up the boiling for the required time we cooled down, brought to the original volume and polarised; the reaction remained perfectly neutral, and we noticed that the inversion became very energetic after the sixteenth hour:—

Hours—								
0	4	8·5	10·5	14	16	18	21·5	25
Polarisation—								
13·25°	11·75°	11·28°	9·11°	4·41°	0·86°	−1·97°	−3·27°	−3·42°

Metal Receivers.—As we have just seen, the inversion is rapid in platinum, even with a very pure water, of which the conductivity did not exceed 1×10^6. In another experiment, after 20 hours and a half we reached a final polarisation of −4·13, while by calculation a total inversion would have been 4·17. However, it is impossible to get theoretical figures on account of the destruction of the fructose which takes place.

To eliminate the action of the air, the experiment was repeated in platinum, but the solution of sugar was covered by a layer of pseudo-cumol. We found that from 11·73 the polarisation altered to − 2·88 after 15 hours, but that the solution became acid. This showed us that the inversion might be due to two causes, either the contact with platinum or on account of the acid formed by the auto-oxidation of the sugar. As to the nature of the metal, it does exercise an influence. We made a series of experiments with vessels of copper, silver, and platinum:—

Time.	Copper.	Silver.	Platinum.
0 hours	11·57°	11·57°	13·25°
4 ,,	11·45	11·56	12·75
8 ,,	10·72	11·0	11·60
12 ,,	7·17	8·98	7·45
16 ,,	0·47	4·40	0·86
18 ,,	1·93	−1·44	−1·97
23·5 ,,	—	−2·95	−3·39
31 ,,	—	−3·59	—

The Influence of Pulverulent Metals.—The experiments made with platinum showed that the platinum metals in a state of fine subdivision should have a very energetic reaction. In a series of flasks of hard glass we placed 50 grms. of a solution of sugar and 1 grm. of metal, and heated on a salt-water bath. Comparative trials were made on the same water-bath, but without the addition of any metal. The following results were obtained :—

Time.	Solution alone.	Palladium.	Platinum sponge.	Rhodium.
0	11·90	11·90	11·90	11·90
4	11·53	−3·45	10·88	9·37
9	9·0	—	4·0	−1·32
12	5·92	—	0·74	−3·04
15	2·32	—	−1·67	−3·72

In these experiments the inversion was more rapid because the water used had a greater conductivity.

The action of palladium is the most interesting, because it was very energetic, and the palladium was able to absorb the gas produced. In a certain number of cases the solution became acid, and formic acid was detected. By forming silver salts of the acids thus obtained and carrying the temperatures to boiling point, carbonic acid was given off; and an odour similar to that of valerianic acid was noticed. Finally, traces of a non-volatile acid were found, but we were not able to identify it.

The study of the electric conductivity of the solution shows that the addition of palladium causes a great diminution of the resistance, and that the reaction goes on, but with less and less energy as time advances.

Temperature also has a great influence on inversion. At 40° and even 60° no inversion takes place, even in the presence of platinum; in fact, the inversion is always weak during the first few hours.

It appears from these experiments that the inversion of sugar by water only in the presence of metals gives a double phenomenon, the hydrolysis of the sugar and the formation of acids at the expense of the molecule of saccharose.

The Influence of Pressure.—Preliminary trials have shown that the inversion of saccharose under great pressure was far less marked than at the atmospheric pressure, and according to special experiments made by the authors on etherification, the latter showed similar results. There would thus appear to be an analogy between the inversion of saccharose by water and the formation of alcoholic ethers.—*Zeits. fur Zuck. Ind. in Bohem.*, p. 234, 1898.

THE EXISTENCE AND DIFFUSION OF GLUCOSE.

By M. BEIJERINCK.

BEIJERINCK describes, under the name of amylases, the enzyms which break up starch; the granulases are amylases which transform starch into maltose and achroodextrine. It is admitted that amylases are easily diffusible bodies. Beijerinck made use of the diffusion of an aqueous solution of amylase in starch and gelatin for the purpose of studying three phenomena of the hydrolysis of starch. The following three methods were used :—

1. Diffusion in solid media to separate the enzyms.
2. The reaction of iodine, to show the formation of achroo- or erythro-dextrine.
3. The development of bacteria in solid media, to prove the presence of sugar as glucose and maltose.

Method of Diffusion.—A 10 per cent aqueous solution of gelatin is prepared, to which ½ per cent of fecula—or, better still, soluble starch—is added. The whole is boiled for a few moments, and then run in very thin layers into well-polished glass dishes; the grain of barley to be examined is cut with a razor down its axis, and the newly cut surface is applied to the gelatin-starch. The two enzyms, maltase and granulase, become diffused, and the limit of the field of diffusion can easily be seen with the naked eye; the plate is then left alone for two days in an

atmosphere of chloroform, to prevent the growth of moulds, after which iodised iodine is poured over the plate. The field of diffusion appears colourless, surrounded by a reddish-violet ring which separates it from the unattacked parts which are coloured blue. Maltase diffuses quicker than granulase, which will explain the existence of the violet ring, due to the presence of erythro-dextrine; in fact, the maltase changes the starch into a mixture of maltose and erythro-dextrine. In the interior of the ring the granulase has changed the erythro-dextrine into malto-dextrine not coloured by iodine, and finally into maltose.

The violet ring is very narrow when we use germinated barley, and, on the contrary, it is very wide when we use non-germinated grains: this shows that granulase does not exist before germination and develops at the same time as the embryon.

Maltose diffuses quickly all over the plate, and cannot be made visible by the auxanographic method.

Glucase transforms maltase into glucase. The latter can be detected on the plate by means of levures which cause the glucose to ferment, but not the maltose; it suffices to mix the cells of these levures with the gelatin, and the colonies formed indicate the presence of glucose.

Auxanogramme.—We prepared a solution of gelatin containing:—

10 per cent of gelatin.
0·5 grm. of acid phosphate of potash.
5 grms. of maltose, dextrine, or ½ per cent of soluble starch.
0·25 grm. of asparagin or 1 per cent of peptone.

If this solution is mixed with a culture of *Sacch. apiculatus*, *fragrans*, or *kefyr*, and then left in a flat glass dish, and afterwards treated with a solution of glucase, a development of levure takes place at the points which are attacked by the glucase: this development is indicated by a well-marked cloudiness forming the auxanogramme of the levure.

If soluble starch has been used, we only find colonies in the immediate neighbourhood of the particles of glucase, on account of these being but very slowly diffused, which is contrary to what happens in the case of the diastase of malt; soluble starch also diffuses very badly. When maltose is used the result is much more easily seen, the sugar diffusing without difficulty.

We also recommend the use of the mycoderm, which developes easily and quickly; it, however, has the inconvenient property of also attacking maltose in the presence of malt peptone, while this action does not take place if we use ordinary peptone, asparagin, or ammoniacal salts.

The glucose of the levure is destroyed at 55°; there appears to be a particular enzym in oats similar to granulase, but we cannot make quite certain that glucase is a chemical entity; on the contrary, it is very probable that there are several modifications in existence, each corresponding to some known grain, such as maize, sorgho, sarrasin, &c.

Beijerinck has studied the three principal species of amylase, according to the products they give with granulose and starch paste; he is of the opinion that, apart from maltose and glucose, three different kinds of dextrine can be obtained—erythro-dextrine, malto-dextrine, or iso-maltose and leuco-dextrine; the first alone gives with iodine a violet colour, the other two have every appearance of the achroo-dextrines. Under the name of leuco-dextrine, the author means a mixture of bodies precipitated by alcohol at 60 per cent from a starch paste, at the moment when colouration by iodine ceases. With concentrated alcohol one obtains malto-dextrine in the form of a syrup. Leuco-dextrine should arise from the cellulose of the starch cell, while granulase should produce erythro-dextrine, malto-dextrine, and maltose. Leuco-dextrine contains a mixture of bodies, some easily diffusible and others exactly the opposite. Leuco-dextrine can, in a neutral or faintly alkaline medium, be converted into maltose by ptyaline or the diastase of the pancreas, while in a faintly acid solution it passes through glucase to the state of glucose.

The breakings-up occur much more slowly with this body than with granulase. The author designates under this name the portion of a solution of starch which is rapidly attacked by the diastase of malt. We can detect two groups of granulases, the acid and the alkaline. To the first group belongs ptyaline and the granulase of pancreas; to the second the granulase of the embryon of barley and wheat, also that of sarrasin, identical with the granulases of the dicoytyles, which are as a rule met with In seedling potatoes and the granulase of the maize germ, &c.

Maltases.—We meet with enzyms of this nature in wheat, barley, rye, and in the organs of a certain number of other vegetables.

Mueder estimated that there would therein be a large number of amylases. Dubrunfaut and Castinier, in 1881, showed that two separate enzyms existed in barley malt. But it is Wysman, with his theory of the two enzyms, who is the most precise. It is, however, necessary to modify his interpretation of the phenomena to some extent.

The dextrinase of Wysman would in fact be, according to Beijerinck, an artificial product resulting from the heating of the amylase of malt for ten minutes at 78°, but it does not actually exist in malt. If we heat the amylase of malt, formed by a mixture of maltase and granulase, to a temperature of 70°, the maltase, which is already weakened at 55°, is completely destroyed, while the granulase only undergoes a slight modification; it partially takes its power of forming maltase, while its faculty of creating dextrine remains intact. The property of liquefying starch paste belongs to granulase, and not to a special enzym.

The author describes his process for the preparation of glucose from maize, making use of the fractional precipitations by means of alcohol.

An interesting point is the transitory formation of dextrine by the glucase acting on the starch paste or on soluble starch; the proof of this is furnished by the auxanographic method in a most ingenious manner. A gelatin plate is prepared, to which has been added *Sacch. ellipsoideus*, but the gelatin only occupies one-half of the plate, and contains 10 per cent of gelatin, 0·5 of soluble starch, 0·25 of asparagin, and 0·005 of phosphate of potassium. The other half of the plate is covered with a similar gelatin, with the exception that it does not contain any starch; glucose is deposited on the two sides of the line separating the two kinds of gelatin. In the first half circle a development of levure is quickly noticed; a little later we also observe a semicircular auxogramme under the glucose in the second half-circle. As a matter of fact, the dextrine first formed by diffusion has spread to the second half, and has been transformed into glucose in the place where it came in contact with glucase.—*Centralblatte fur Bakteriologie*, ii., p. 221, 1897.

A COLLECTOR FOR DISTILLATION OF AMMONIA FROM WATER.

By F. P. DUNNINGTON.

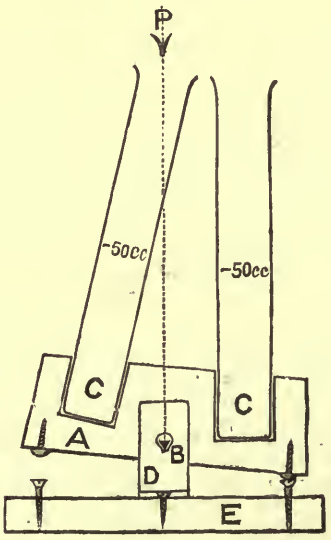
In the familiar process of making a determination of free and albumenoid ammonia in water, the close attention which is demanded to change the receptacle as each of the several portions of 50 c.c. is collected, is somewhat engrossing to anyone when conducting other analytical work. To avoid this embarrassment I have devised the following simple apparatus, which, for lack of a better name, is called a collector.

The figure presents a section of one-fourth size. From

this the arrangement and working of the apparatus may be understood. It is made as follows:—

In a block of dry poplar or other light wood, A, 43 × 53 × 150 m.m., a hole of 3 m.m. diameter is made at B for the pivot, and the large holes, C C, for Nessler tubes, are placed at the same distance from the centre of the block and equally inclined, as indicated. When the Nessler tubes are 29 m.m. in diameter, these holes should be about 31 m.m. and be lined with a strip of woollen cloth to afford a snug fit for the tubes. The pivot B is a knife edge, made by grinding at its ends, a piece of a double three-inch saw file about 55 m.m. long, and is merely hammered into the small hole cut for it. The knife edge is supported by a pair of plain two-inch angle irons (such as are kept in stock at a hardware store); in each of these, the hole in the upright limb is bored out and filed to the shape shown in the figure. These irons, D, are screwed to the wooden base, E, 170 × 170 × 20 m.m.

The motion of the block A is checked by two round-head screws fastened into the under side of A, and by two flat-head wood screws partly screwed into the block E. By screwing the latter up or down you may adjust the



apparatus so that when one tube is empty and the other is being filled, as soon as the latter collects 50 c.c. of water, it topples over and immediately brings the other tube under the point P, to collect the distillate. While the second tube is being filled, you may hold the block A, remove the first tube and empty or replace it by another tube of same size and weight; when the second tube has collected 50 c.c. it will topple over and again bring the mouth of the empty tube under P. The screw which serves to fasten each angle iron in place also passes through one end of a slip of thin sheet brass 15 × 30 m.m., the other end of which is bent up at right angles, so serving to keep the pivot from shifting to one side, but not binding upon it. This piece of brass is not shown in the figure, since it would cover the pivot end.

The Nessler tubes used are 29 m.m. in diameter and 195 m.m. long, and weigh 49 grms.; should the tubes be heavier, it would be necessary to bore the hole for the pivot at a point a little higher up on the centre line of the block A. It is easy to adjust this apparatus so that the amount required to topple the tubes will not vary as much as one-half c.c. from the 50 c.c.—*Journal of the American Chemical Society*, vol. xx., No. 4.

A REDUCTION OF PERMANGANIC ACID BY MANGANESE PEROXIDE.*

By H. N. MORSE and C. L. REESE.

(Concluded from p. 79).

THE next series of experiments was designed to determine the relative rates of reduction when equal volumes of permanganic acid are agitated, on the one hand, with a given volume of hydrogen, and on the other, with a quantity of the peroxide which is equal to that which should be produced by the absorption of the hydrogen. Here, again, the three solutions, A, B, and C, were employed in the comparison.

The quantities of permanganate to be reduced were in all cases 20 c.c. In addition to this, there was added to the hydrogen tubes a quantity of permanganate which would dispose of the gas in accordance with the equation $HMnO_4+3H=2H_2O+MnO_2$, and to the other tubes enough permanganate and manganous sulphate to produce the same amount of oxide as would result from the absorption of the hydrogen according to the equation $2KMnO_4+3MnSO_4+2H_2O=2HKSO_4+H_2SO_4+5MnO_2$. In adding the acid, account was taken of the fact that, in the case of those tubes in which the peroxide was produced by the action of the manganous salt on the permanganate, a portion of the required acid had already been introduced through the sulphate.

In order that the quantity of the gas introduced might be accurately measured, the tubes designed to receive the hydrogen were drawn out—at one end to a capillary, and at the other to a narrow neck—just wide enough to permit the introduction of liquids from a burette. After introducing the permanganate and the calculated amount of sulphuric acid, the larger passage was closed before the blast-lamp. The capillary end was then attached to a Hempel burette filled with mercury, and a volume of air was withdrawn from the tube which was equal to that of the hydrogen to be introduced. The burette was then replaced by one containing hydrogen. By careful manipulation no especial difficulty was experienced in introducing quite exactly the required volume of gas. To prevent the possibility of an explosion of the mixture of gases while closing the capillary, the tube was so inclined during the operation that the liquid in the tube covered the inner end of the narrow passage. It is hardly necessary to state that, in estimating the volume of gas required for an experiment, proper corrections were made for temperature, pressure, and water vapour.

Through the addition of sulphuric acid to all of the tubes, and of a standard solution of manganous sulphate to a portion of them, the original permanganate solutions were somewhat diluted, and those portions to which the manganous sulphate was added, to a greater extent than the others; hence, in order to equalise the conditions as to concentration, it was necessary to introduce a certain amount of water into the tubes in which the permanganate was to be agitated with hydrogen.

The tables which follow give the molecular ratio of the permanganic acid to be reduced to the oxide, the relation of the acid to the potassium of the permanganate, the time of agitation, the percentage reduction of the acid to peroxide, and the volumes of oxygen which were estimated to have been lost.

Permanganate Solution A.

1 c.c. equivalent to 5 m.grms. of iron.
Volume of original solution to be reduced = 20 c.c.
Volumes of hydrogen used = 7·5 c.c.
Molecular ratio of $HMnO_4 : MnO_2$ = 20 : 12·5.

It should be remarked with regard to the above, as well as all following similar data that, of the figures expressing reduction of permanganic acid, only those on the same horizontal line are safely comparable. This is true even when the time of agitation is the same in successive

* From the *American Chemical Journal*, xx., No. 7.

Acid.	Time.	Decomposition by MnO_2 from $MnSO_4$.	Volume of oxygen liberated.	Decomposition by MnO_2 from H_2.	Volume of oxygen liberated.
	Hours.	Per cent.	C.c.	Per cent.	C.c.
K	150	13·75	0·83	9·59	0·58
K	150	16·50	0·99	8·55	0·51
K	300	21·67	1·29	10·25	0·62
K	600	40·00	2·40	14·34	0·86
2K	150	21·35	1·28	11·60	0·70
2K	150	17·65	1·06	14·00	0·74
2K	300	28·33	1·70	17·00	1·02
2K	300	28·33	1·70	16·67	1·00
2K	600	41·66	2·50	21·08	1·27
3K	150	15·16	0·91	15·83	0·95
3K	150	14·67	0·88	13·50	0·81
3K	300	26·34	1·58	20·83	1·25
3K	300	23·90	1·43	20·74	1·25
3K	600	44·91	2·70	27·00	1·62
3K	24	6·67	0·40	Hydrogen not all absorbed.	—
3K	24	5·25	0·32	,,	—

experiments, unless the agitation happened to be simultaneous. The rate of the reduction appears to be influenced even by such changes of temperature as are experienced in the laboratory, as, for instance, between day and night.

Permanganate Solution B.

1 c.c. equivalent to 10 m.grms. of iron.
Volume of original solution to be reduced = 20 c.c.
Volumes of hydrogen used = 15 c.c.
Molecular ratio of $HMnO_4 : MnO_2 = 20 : 12·5$.

Acid.	Time.	Decomposition by MnO_2 from $MnSO_4$.	Volume of oxygen liberated.	Decomposition by MnO_2 from H_2.	Volume of oxygen liberated.
	Hours.	Per cent.	C.c.	Per cent.	C.c.
3K	150	17·5	2·1	28·25	3·39
3K	150	15·08	1·81	27·33	3·21
3K	150	17·17	2·06	28·25	3·39
3K	300	33·17	3·98	31·75	3·80
3K	300	32·93	3·95	32·68	3·92
3K	600	61·59	7·38	43·75	5·25
3K	600	62·50	7·50	41·83	5·02
6K	150	18·18	2·18	32·50	3·90
6K	150	19·34	2·32	31·83	3·82
6K	150	20·18	2·42	35·08	4·21
6K	300	31·75	3·81	36·00	4·31
6K	300	31·75	3·81	37·08	4·45
6K	600	60·75	7·28	44·00	5·29
6K	600	75·75	9·08	46·43	5·57
3K	24	3·33	0·40	8·58	1·03
3K	24	4·00	0·48	10·67	1·28

Permanganate Solution C.

1 c.c. contained 51 m.grms. $KMnO_4$=89·38 m.grms. Fe.
Volume of original solution to be reduced = 20 c.c.
Volumes of hydrogen used = 40 c.c.
Molecular ratio of $HMnO_4 : MnO_2 = 20 : 3·784$.

Acid.	Time.	Decomposition by MnO_2 from $MnSO_4$.	Volume of oxygen liberated.	Decomposition by MnO_2 from H_2.	Volume of oxygen liberated.
	Hours.	Per cent.	C.c.	Per cent.	C.c.
K	150	9·68	10·48	19·93	21·58
K	150	13·75	14 90	19·93	21·58
K	300	22·59	24·38	21·58	23·39
K	300	17·00	18·42	21·75	23·57
2K	150	11·83	12·82	22·50	24·38
2K	150	12·68	13·73	23·93	25·92
2K	300	16·65	18·06	22·08	23·93
2K	300	20·93	22·66	23·33	25·28
3K	150	13·50	14·63	23·74	25·74
3K	150	12·93	14·00	25·83	27·99
3K	300	17·75	19·23	26·75	28·90
3K	24	2·50	2·71	19·58	21·22
3K	24	2·50	2·71	20·18	22·85

The relation of the reduction of the permanganic acid to the time of agitation, as well as to the acidity of the solutions, will be made clearer by the following arrangement, in which the means are given in the case of duplicated determinations:—

Solution A.

1. Oxide from $MnSO_4$.

	24 hours. Per cent.	150 hours. Per cent.	300 hours. Per cent.	600 hours. Per cent.
Acid = K	—	15·13	21·67	40·00
,, = 2K	—	19·50	28·33	41·66
,, = 3K	5·96	14·92	25·12	44·91

2. Oxide from H_2.

Acid = K	—	9·07	10·25	14·34
,, = 2K	—	12·08	16·84	21·08
,, = 3K	Hydrogen not all absorbed.	14·67	20·79	27·00

Solution B.

1. Oxide from $MnSO_4$.

Acid = 3K	3·67	15·56	33·05	62·00
,, = 6K	—	19·23	31·75	68·27

2. Oxide from H_2.

Acid = 3K	9·63	27·94	32·22	42·79
,, = 6K	—	33·14	36·54	45·22

Solution C.

1. Oxide from $MnSO_4$.

Acid = K	—	11·72	19·75	—
,, = 2K	—	12·26	18·75	—
,, = 3K	2·50	13·22	17·75	—

2. Oxide from H_2.

Acid = K	—	19·93	21·67	—
,, = 2K	—	23·22	22·71	—
,, = 3K	19·88	24·82	26·75	—

An examination of the preceding table for the purpose of comparing the efficiency of manganous sulphate and hydrogen as oxygen liberating agents, shows that, in the case of solutions B and C, the latter is much more active than the former during the first twenty-four hours—that is, during the period of, or immediately following, the formation of the peroxide which results from the absorption of the gas. This is apparently not true of the very dilute solution A; for, in the experiments upon it, a somewhat smaller reduction of the acid was found than would have been accounted for by the complete absorption of the hydrogen. It cannot, however, be affirmed that the quantity of oxygen liberated was less, in proportion to hydrogen absorbed, in A than in B and C. This is one of the questions to which it is hoped to give further attention in the future. The maximum efficiency of the hydrogen as a quickly acting oxygen-liberating agent, appears to be reached in the case of the nearly saturated solution C, in which the mean reduction during the first twenty-four hours amounted to 19·88 per cent, as against 2·5 per cent for the manganous sulphate. We call attention to the fact—also noticeable in the results of Messrs. Meyer and Von Recklinghausen—that the reduction of 19·88 per cent signifies the liberation of 22 c.c. of oxygen, a volume which is nearly one-half that of the hydrogen (40 c.c.) employed in all the experiments with the solution C.

During the period from twenty-four hours to one hundred and fifty hours, the oxide produced by hydrogen acted much less rapidly in C than the oxide from the manganous salt. In B—and possibly also in A—the order of efficiency appears to be reversed, the oxide from the hydrogen being the more active one. The latter fact was interesting to us, because it may possibly throw some light upon the important question, whether the phenomenal liberation of oxygen which is observed when hydrogen or carbon monoxide acts upon permanganic acid, *attends the absorption*

of the gas or follows the formation of the oxide produced by the absorption of the same; and it suggests a line of investigation which we hope to pursue.

During the period from one hundred and fifty to three hundred hours—also during that from three hundred to six hundred hours, wherever the agitation was so long continued—the oxide from the hydrogen was decidedly less active than that from the sulphate. In one instance, in which a portion of the solution C had been agitated with hydrogen for three hundred hours, a smaller reduction was found than had occurred in similar experiments during an agitation of one hundred and fifty hours. This discrepancy was explained at the time by the low temperature which prevailed during the agitation of the tube whose contents showed the low reduction.

Assuming that liberation of oxygen in solutions of permanganate or permanganic acid is in general due to the presence of suspended oxide, there is no evidence to be found in our results that the reaction has a limit, as believed by Messrs. Meyer and Von Recklinghausen. The evidence to the contrary is very clear in all cases in which the suspended oxide was prepared from manganous sulphate, and also in those cases in which the oxide from hydrogen acted upon solutions A and B. The reduction accomplished in C by the oxide from hydrogen is apparently small during the twenty-four to one hundred and fifty hour and the one hundred and fifty to three hundred hour periods. It is, however, unmistakable, except in the one case which has already been explained. That the percentage reduction for equal periods of time after the first twenty-four hours should be smaller throughout in C than A and B, is easily accounted for by the fact that the suspended oxide in C was relatively less than one-third of that in A and B.

The work which we have here described is only a fragment of a proposed investigation of the reduction of permanganic acid by the peroxide of manganese. The results obtained are not decisive; nor are they even strikingly important in their direct bearing on the question of the cause of the difference between the action of gaseous and liquid reducing agents on permanganic acid. They do, however, suggest certain possible methods of solving the problem.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 79).

Maganese, Nickel, Cobalt, Copper, Zinc.

Ammonia is added to the flask containing manganese, the earths, &c., and hydrogen sulphide gas is introduced, whereby manganese, nickel, copper, zinc, and a small part of the platinum from the dish are precipitated. The flask is set aside, corked for at least twelve hours, and preferably twenty-four, or even longer; the precipitate, collected and washed on a small filter with water containing ammonium chloride and sulphide, is extracted by hydrogen sulphide water acidified with one-fifth its volume of hydrochloric acid (sp. gr. 1·11), manganese and zinc, if present, going into solution.

Manganese.—The filtrate is evaporated to dryness, ammonium salts are destroyed by evaporation with a few few drops of sodium carbonate solution, hydrochloric and a drop of sulphurous acid are added to decompose excess of carbonate, and to dissolve precipitated manganese, and the latter is re-precipitated boiling by sodium carbonate after evaporation of the hydrochloric acid. If zinc is present it can be separated from the manganese after weighing. For the small quantities of manganese usually found the sodium carbonate method of precipitation is to be preferred to that by bromine or sodium phosphate, as equally accurate and a great time saver. No precipitations have as yet been made with hydrogen peroxide in alkaline solution, in the manner proposed by Jannasch and Cloedt (*Zeitschr. für Anorg. Chemie.*, vol. x., p. 405, 1895), but the method appears full of promise and extremely simple, affording also separation from zinc, if present, and it will be subjected to full trial at some future time.

The employment of ammonium sulphide instead of bromine for the separation of manganese from the alkaline earths and magnesia has the advantage that, by a single operation, nickel, copper, and zinc are likewise removed if present. There need be no fear of overlooking nickel or copper, for under the conditions of the precipitation they are not held in solution. Now and then a trace of alumina may be found in the precipitate, and magnesia, too, would contaminate it if ammonium salts were not present in sufficient quantity. Regard must therefore be had to these possibilities, and also to the rather remote possibility of the presence of rare earths which were not thrown out by the basic acetate precipitation (see footnote, p. 81).

Nickel, Cobalt, Copper.—The paper containing these is incinerated in porcelain, dissolved in a few drops of aqua regia, evaporated with hydrochloric acid, the copper and platinum thrown out warm by hydrogen sulphide, and nickel and cobalt thrown down from the ammoniacal filtrate by hydrogen sulphide. This is then rendered faintly acid by acetic acid and allowed to stand. The sulphide of nickel is simply burned and weighed as oxide, its weight being almost always very small, and then tested for cobalt in the borax bead.

It is somewhat unsafe to consider traces of copper found at this stage to belong to the rock if the evaporations have been conducted, as is usually the case on a copper water-bath, or if the water has been used which has been boiled in a copper kettle, even if tinned inside. Therefore, and because of its contamination by a little platinum, it is better to determine copper in a separate portion if its presence is indicated with certainty.

Calcium and Strontium (Barium).

Precipitation and Separation.—The platinum derived from the dish in the silica evaporation, except for the small portion precipitated with the manganese sulphide, is now wholly in the filtrate from the latter. Its filtration at this or any other stage is quite unnecessary; nor is the removal of ammonium chloride usually demanded, since there is no undue amount present in most cases, the first precipitation of alumina, &c., having been by sodium acetate.* Therefore, without destroying ammonium sulphide the calcium and strontium are thrown out by ammonium oxalate at boiling heat, the precipitate, often darkened by deposited platinum sulphide, is ignited and re-dissolved in hydrochloric acid, boiled with ammonia to throw out traces of alumina sometimes present, and re-precipitated as before, but in a small bulk of solution. It is weighed as oxide, transferred to a small flask of 20 c.c. capacity, dissolved in nitric acid, evaporated to dryness at 150° to 160° C., and the separation of strontium from calcium effected by ether-alcohol† or amyl alcohol (Browning, *Am. Journ. Sci.*, Series 3, vol. xliii., pp. 50, 314, 1892).

Behaviour of Barium.—Barium will, after two ammonium oxalate precipitations, never be found with the ignited calcium and strontium in more than spectroscopic traces, unless originally present in excess of 3 or 4 milligrms., and very often only when in considerable excess (W. F. Hillebrand, *Journ. Am. Chem. Soc.*, vol. xvi.,

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

* If two or three precipitations by ammonia alone are depended on, the second and third filtrates are evaporated rapidly to dryness and the ammonium salts removed by ignition.

† See Fresenius, *Zeitschr. für Anal. Chemie*, vol. xxxii., pp. 189, 312, 1893, for the latest improvement in this method.

p. 83, 1894; Chemical News, vol. lxix., p. 147, 1894). If present with them, however, it will be separated with the strontium by ether-alcohol or amyl alcohol, and these two must then be treated by the ammonium chromate method as prescribed by Fresenius (*Zeitschr. fur Anal. Chem.*, vol. xxxix., p. 428, 1890), in order to arrive at the strontium. The barium is best estimated in a separate portion (see Barium).

Necessity of two Precipitations by Ammonium Oxalate.—It may be said with regard to the separation of calcium from magnesium, that two precipitations by ammonium oxalate are essential to the attainment of correct results, not only for the complete removal of magnesium but of sodium as well, the retention of compounds of the latter element by calcium oxalate having been frequently observed here and elsewhere.

Magnesium.

Platinum sulphide strongly contaminates the precipitate of magnesium phosphate in the first filtrate from the calcium oxalate, unless ammoniacal salts have been removed, as is advisable with very little magnesium; but this matters not, as it remains on the filter when the phosphate is re-dissolved in hydrochloric acid and added to the second filtrate from calcium oxalate, where it is again precipitated. Barium phosphate will not contaminate the second precipitate unless there are notable amounts of barium in the rock, in which case it must be removed by sulphuric acid prior to the final precipitation of the magnesium. The magnesium-ammonium-phosphate may be collected in a Gooch crucible and weighed, or on a paper filter, whence it may be washed into a tared crucible by nitric acid, evaporated,* ignited, and weighed therein as pyrophosphate. The latter way, though longer than that by the Gooch crucible, offers a certain advantage in facilitating the detection and estimation of the small amount of calcium which the magnesium always carries with it (see below), but it suffers from an objection which will appear shortly. In order to get the calcium which it carries the ignited pyrophosphate is dissolved in a few drops of hydrochloric acid, the solution is rendered just ammoniacal, the precipitate just re-dissolved by acetic acid, and a very small pinch of ammonium oxalate is added. In the cold solution, kept down to a few cubic centimetres in bulk, a turbidity appears shortly, which is almost invariably calcium oxalate, sometimes accompanied by magnesium oxalate. If necessary, it can be purified by re-solution and re-precipitation after ignition, and its weight, averaging one-half milligrm., is then added to that of the lime already found, and subtracted as tricalcium phosphate from that of the magnesium pyrophosphate, in order to arrive at the true figure for magnesium. This separation, to be successful, must be done with care.

Now it has been often observed that the pyrophosphate obtained by evaporation with nitric acid in a platinum crucible does not always dissolve completely in hydrochloric acid after ignition, but that sometimes a white residue is left in light lumps which appear to be quite insoluble in acids. It contains no silica, but only phosphoric acid and magnesia, apparently, and is presumably a peculiar metaphosphate. The cause of its formation is probably this: In the evaporation with nitric acid magnesium nitrate and free phosphoric acid are formed, and crystallisation partially takes place before the phosphoric acid has had a chance to expel the nitric acid, the consequence being that the complete molecular re-arrangement from which only pyrophosphate can result on ignition, can not take place, and the ignition product contains, in addition to pyrophosphate, other compounds, including, perhaps, metaphosphate and metaphosphoric acid. If the last, the weight found would be in error by the water retained by the metaphosphoric acid, even supposing none of the latter to be volatilised during ignition. Otherwise the weight would not differ from that of pyrophosphate alone. The uncertainty seems to be sufficient to condemn the method for accurate work, which is unfortunate, for it obviates the need of dissolving the phosphate off the felt of the Gooch crucible and subsequent concentration of the filtrate in order to look for contaminating lime.

Barium and Titanium.

Barium.—It has been said above (see preceding col.) that only in very exceptional cases will barium be found with the calcium and strontium after two, or possibly three, precipitations of the latter as oxalate, since it passes into the filtrates with the magnesium, whence it may be obtained as sulphate after the removal of ammoniacal salts. Addition of some alcohol insures also the recovery of traces of strontium if the rocks are very rich in it. But it is unsafe to regard the amount thus separated from the magnesium as representing the total amount of barium in the rock. It will almost always be found lower than the truth, probably for the reason that there are opportunities during the analysis for slight losses in the form of sulphate. It is best to estimate it in a separate portion, which may also serve with advantage for the estimation of titanium.

The powder is attacked by hydrofluoric and sulphuric acids, and every trace of the former then expelled by repeated evaporations with the latter. This expulsion of fluorine must be thorough, or else the titanium result will be low, and it is not always easy to effect this complete removal, though the time required seems to be in no slight degree dependent on the nature of the fluorides to be decomposed. Long after every trace of fluorine seems to be gone, the formation of a crust on the evaporating salts sometimes allows an accumulation of enough hydrofluoric acid gas to become plainly manifest to the smell on breaking the crust. Possibly fusion of the mixed sulphates and fluorides with boric acid, and removal of the latter by evaporations with methyl alcohol saturated with dry hydrochloric acid gas, as recommended by Jannasch (*Zeitsch. fur Anorg. Chemie.*, vol. xii., p. 223, 1896), for the conversion of sulphates and possibly fluorides into soluble chlorides, would effect this expulsion of fluorine more certainly than mere evaporation with sulphuric acid; but these operations evidently require almost constant personal supervision, whereas repeated evaporations with sulphuric acid can be carried out on a radiator with almost no supervision. Moreover, the barium would have to be re-precipitated, whereas by the sulphuric-acid method it is already as sulphate.

The sulphate residue is digested for some time with dilute sulphuric acid of not less than 5 per cent strength. With acid rocks solution is very complete, but it can be made nearly so with even the most basic by transference to a small beaker and boiling. The filtrate is set aside, the residue ignited and fused with sodium carbonate, since zircon, andalusite, and a few other minerals are incompletely decomposed by hydrofluoric acid, and zircon, at least, is often present in appreciable amount. The melt is leached with water, washed, and extracted by a few drops of dilute hydrochloric acid, from which solution the barium is thrown out by a large excess of sulphuric acid. A single solution of the barium sulphate in concentrated sulphuric acid and re-precipitation by water suffices to remove traces of calcium which might contaminate it if the rock was one rich in calcium, and even strontium is seldom retained by it in quantity sufficient to be concerned about. Should this be the case, however, which will occur when the SrO and BaO are together in the rock in, roughly speaking, 0·2 and 0·4 per cent respectively, the only satisfactory way is to convert the sulphates into chlorides and to apply to the mixture the ammonium chromate method of separation (see *ante*).

Barium and strontium sulphates can be brought into a condition for testing spectroscopically by reducing for a very few moments the whole or part of the precipitate on

* A pink colour of varying intensity almost invariably becomes apparent as the mass approaches dryness, a most delicate test for the traces of manganese which always escape precipitation by ammonium sulphide or bromine.

a platinum wire in the luminous tip of a Bunsen burner, and then moistening with hydrochloric acid. This should be known to everyone, but probably is not.

The procedure outlined in the foregoing paragraphs for the estimation of calcium, strontium, and barium in silicate rocks is the one which long experience has shown to be best adapted for securing the most satisfactory results with a minimum expenditure of time (for details consult W. F. Hillebrand, *Journ. Am. Chem. Soc.*, vol xvi., p. 83, 1894; Chemical News, vol. lxix., p. 147, 1894). Even where no attempt is made to separate contaminating traces of SrO and BaO one from the other, the error is usually of no great consequence, for an absolute error of 25 per cent, even in a substance constituting only one or two tenths per cent of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

Separation of Barium from Calcium and Magnesium by the Method of Mar.—With such small amounts of barium as are usually found in rocks it is doubtful if Mar's (*Am. Journ. Sci.*, Series 3, vol. xliii., p. 521, 1892) method for the separation of barium from calcium and magnesium, by the solvent action of concentrated hydrochloric acid mixed with 10 per cent of ether on the chlorides, could be conveniently applied here, although for larger amounts the method would seem to be accurate, and easily executed. Moreover, it would probably not entirely remove contaminating strontium, and hence offers no advantage.

Titanium: Colorimetric Method.—The small hydrochloric filtrate from the barium sulphate, above mentioned, is evaporated to expulsion of the hydrochloric acid and added to the main solution containing the titanium, which is then oxidised by fluorine-free hydrogen peroxide (W. F. Hillebrand, *Journ. Am. Chem. Soc.*, vol. xvii., 1895; Chemical News, vol. lxxii., p. 158, 1895), and compared with a standard solution of titanium sulphate, similarly oxidised (Weller's method) (*Ber. Deutsch. Chem. Gesell.*, vol. xv., p. 2593, 1882). Mere traces of hydrofluoric acid render the results inaccurate; hence the caution enjoined as to the first treatment of the rock powder and as to the character of the hydrogen peroxide, which, as sold in the market, often contains fluorine.

Dunnington (*Journ. Am. Chem. Soc.*, vol. xiii., p. 210, 1891) has pointed out the necessity for the presence of at least 5 per cent of sulphuric acid in solutions which are to be thus tested for titanium, in order, as he concludes, to prevent partial reversion to metatitanic acid, which does not give a colour with hydrogen peroxide. The standard solution of titanium sulphate holding conveniently about 1 centigrm. TiO_2 in 10 c.c., equivalent to 1 per cent of TiO_2 in 1 grm. of rock, contains, therefore, 5 per cent or more of sulphuric acid. Of this, 10 c.c. are mixed with a sufficiency of hydrogen peroxide (2 c.c. of most commercial brands is ample) and diluted to 100 c.c. in a measuring flask.

The solution to be tested, evaporated if necessary to less than 100 c.c., is now to be fully oxidised, and if the colour is less intense than that of the standard, is made up to 100 c.c. with dilute sulphuric acid in a measuring flask, and mixed, otherwise in a flask of sufficient size to insure that its colour shall be less intense. If rectangular cylinders are used for comparison, there should be a light box, blackened inside and provided with one ground-glass end against which the cylinders can be sunk from an opening above, the other end being open for the observer to look through. One cylinder being filled with the solution to be tested, 10 c.c. of the diluted standard are run into the other from a burette, and water is added from a second burette until there is no distinction as to colour. A second and a third portion of the standard can be run in and diluted, and the mean of several determinations struck, when a simple calculation gives the percentage of TiO_2 in the rock.

If the convenient but expensive Soleil-Duboscq colorimeter is used, or the simple Nessler tubes, it is of course unnecessary to dilute the rock solution to the extent above required, should it be stronger than the standard. Experience has shown, however, that differences can not be sharply estimated in strongly coloured solutions, and that the results are much more satisfactory when the colour intensity is not much, if any, greater than that given by a standard of the above concentration. For the percentages of titanium found in rocks, clays, and soils, usually under 1 per cent, but rising to 2 or even 3 per cent or more occasionally, the colorimeter method gives results which are fully equal to those of the best gravimetric method, besides being a great time saver. The error introduced by iron, in consequence of the yellowish colour of its sulphate solution, is practically negligible unless its percentage is very high; then either the iron must be removed prior to making the colour test or, possibly better still, correction should be applied for known amounts of ferric sulphate in solutions of the requisite dilution.

The exact correction to be applied in such cases is difficult of determination because of the impossibility of matching the colours of titanium peroxide solutions with those of ferric sulphate; but tests made go to show that the colouring effect of 0·1 grm. of Fe_2O_3 in 100 c.c. 5 per cent sulphuric acid solution is about equal to 0·2 m.grm. of TiO_2 in 100 c.c. when oxidised by hydrogen peroxide. This amounts to a correction of only 0·02 per cent on 1 grm. of rock containing the unusual amount of 10 per cent Fe_2O_3.

Gooch's Method not readily Applicable to Rocks Containing Zirconium.—Prior to the adoption of this method, the excellent one of Dr. Gooch (*Proc. Am. Acad. Arts Sci.*, N.S., vol. xii., p. 435; *Bull. U.S. Geol. Survey*, No. 27, p. 16; Chemical News, vol. lii., pp. 55 and 68, 1885), was invariably used in this laboratory. Occasional inability to secure clean and complete precipitations by it was experienced, especially with a certain series of rocks rather poor in titanium. Long research showed the difficulty to be due to the presence of zirconium, which acts as a marked preventive of the precipitation of titanium by boiling in an acetic acid solution. The above rocks were found to contain up to 0·2 per cent of ZrO_2, and this amount was able to prevent precipitation of 0·3 per cent of TiO_2. The titanium which came down in excess of this amount did not settle out in flocculent condition, as happens when zirconium is not present, and it was difficult to filter. After the removal of the zirconium, however, no difficulty was experienced in precipitating all the titanium with the usual ease. In view of the good results obtainable by the colorimeter method in the presence, and by the Gooch method in the absence, of zirconium, it is incomprehensible that the old method of precipitation by many hours boiling in a nearly neutral sulphate solution in presence of sulphurous acid should still find adherents in any part of the world.

Baskerville's Method.—Baskerville (*Journ. Am. Chem. Soc.*, vol. xvi., p. 427, 1894), has proposed the separation of titanium from iron and aluminum by boiling the neutralised solution of the chlorides for a few minutes in presence of sulphurous acid. The test separations, as given by him, are sharp, and a single precipitation is said to suffice, the titanium being found free from iron and easily filterable. If it is desired to determine TiO_2 gravimetrically, this method seems admirably suited. Zirconium would probably be likewise precipitated (see *prox.*), and phosphorus, perhaps, also; but this last point has not been investigated.

(To be continued).

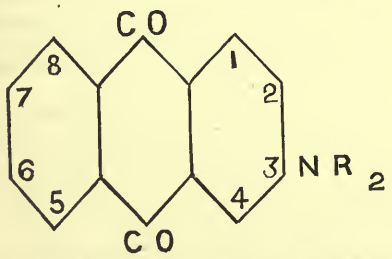
The Molecular Transposition of the Ethers of some Iso-aldoximes. — C. Neubauer. — β-Mononitrobenzaldoxime gives, with the mononitrobenzaldehyd in alcoholic solution, mononitrobenzyl-mononitro-isobenzaldoxime, $C_{14}H_{11}N_3O_3$. Benzyliso-œnantaldoxime, $C_{14}H_{21}NO$, which melts at 78°, undergoes only a doubtful transformation, or even none at all. A number of other bodies are described, and the author finishes with a few remarks on the preparation of benzhydroxylamine.—*Liebig's Annalen.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 22, May 31, 1898.

The Preparation and Properties of the Dialcoyl-amido-anthraquinones-3.—A. Haller and A. Guyot.—The authors have already shown that the substituted orthobenzoylbenzoic acids are transformed by the influence of reducing agents, first into substituted monophenylphthalides, and then into the benzylbenzoic derivatives. They have now endeavoured to condense these acids into anthraquinonic compounds by the method used for producing analogous compounds with the benzoylbenzoic acids. By heating dimethyl-anidised acid with concentrated sulphuric acid at 175°—180° sulphurous acid is given off, and eventually—after precipitation, washing, &c.—beautiful red needles are formed, melting at 181°. Besides this dimethylamidoanthraquinone, there are always present badly-defined products of oxidation. These have been studied, with the result that the method adopted for the condensation has been modified. The new anthraquinonic derivatives can only have the following constitution:—

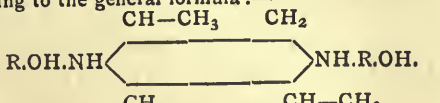


They lend themselves very readily to the preparation of a group of nitrated, amidised, sulphonated, and hydroxylised derivatives, of which some may be applied to the arts.

Action of some Carbonates on Chromous Acetate.—G. Bauge.—Already inserted in full.

The State of Equilibrium of the Ternary System: Lead—Tin—Bismuth.—Georges Charpy.—These three metals are capable of mixing in all proportions, and form at the requisite temperature a homogeneous liquid; they do not form definite compounds or isomorphous solutions, solids, or mixtures. They therefore correspond to the simplest case that can be presented from the point of view of chemical equilibrium. The composition of any such an alloy can be shown diagrammatically by means of the Thurston triangle. A point taken within this triangle represents the ternary alloy which contains quantities of the three metals proportional to the distances of this point from the three sides of the triangle. Here a good deal of mathematics follows.

On Dimethylpiperazine and some Phenolic Combinations of this Base.—P. Cazeneuve and M. Moreau.—When heated in alcohol at 93°, molecule for molecule, under the same conditions as piperazine, dimethylpiperazine disengages carbonic acid at the expense of the phenolic carbonates, and we finally obtain, instead of urethanes, diphenolic combinations of the base corresponding to the general formula:—



In this manner the authors obtained the diphenate, digaïacolate, and the dinaphtholates α and β of dimethylpiperazine. This new base, by reason of its recent introduction into therapeutics (lycetal, or tartrate of dimethylpiperazine), merits further study, so that its properties may the better be understood.

Heats of Neutralisation of Phenylphosphoric Acid.—G. Belugou.—The product of the reaction of phosphoric anhydride on phenol is dissolved in water and washed with ether to remove the diphenyl-phosphoric acid. The aqueous solution is treated with acetate of lead. Fractional precipitations enable us to separate the phosphoric acid, which is the first precipitated. The monophenyl phosphate of lead, which is next formed, is suspended in water and decomposed by sulphuretted hydrogen. By adding small portions of the salt to a known volume of water the richness of the solution can be determined by simple acidimetry; when the solution contains 1 molecule of phenylphosphoric acid per 6 litres it is neutralised and the carbon determined.

Some Halogen Derivatives of Ethylphenylketone.—A. Collet.—The halogen derivatives described in this note were obtained by the action of the chlorides of propionyl and of α-bromoproprionyl on monochlorised or monobromised benzene in the presence of $AlCl_3$. The operation is conducted in the same manner as in the case of the halogen derivatives of methylphenylketone. Four of these derivatives are fully described, viz., ethyl-*p*-chlorophenylketone, ethyl-*p*-bromophenylketone, bromoethyl-*p*-chlorophenylketone, and bromoethyl-*p*-bromophenylketone.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xix.-xx., No. 8.

Conductivity of Electrolytes in Organic Solutions.—P. Dutoit and L. Friderich.—A very long paper, in which the authors describe a number of experiments with various organic substances; they finally conclude that the values $\mu\infty$, furnished by the same electrolyte dissolved in different solvents, are in direct function of the degree of polymerisation, and in inverse function of the coefficient of viscosity of these solvents.

Speed of Limited Reactions.—P. Th. Muller.—A chemical reaction is limited when it stops before the whole of the substance theoretically transformable has undergone the change indicated by the chemical equation. The authors have studied the subject of etherification of acetic acid and alcohol in equivalent quantities at the ordinary temperature, also by Knoslauch's method, as well as that of saponification; these are all treated mathematically, but, the authors add, it does not appear possible to represent all cases of etherification by formulæ when the reaction is between equivalent quantities of acids and alcohols; the acid plays a preponderating part and the equilateral hyperbola proposed by M. Berthelot shows the speed of the reaction with the greatest fidelity.

Absorption of Nitric Oxide by Ferrous Salts.—V. Thomas.—Already inserted in full.

The Action of the Bacteria of Sorbase on the Plurivalent Alcohols.—G. Bertrand.—It has already been shown by the author that sorbite can be transformed into sorbase by the action of a particular bacterium. MM. Vincent and Delachanal have, with the same bacterium, obtained levulose from mannite. These two tranformations are absolutely comparable; they correspond to the production of a ketose by the oxidation of a secondary alcoholic grouping of the primitive body, and the same formula of the reaction serves to represent them both. The plurivalent alcohols experimented on are divided into two groups; some—such as glycol, xylite, and dulcite—resist the oxidising action, while others on the contrary—particularly glycerin, sorbite, and mannite, of which the coefficient of carbon is a multiple of three—contribute in a most efficacious manner to the growth of the microbe, at the same time losing 2 atoms of hydrogen, forming, besides the two bodies already mentioned, erythrite, arabite, volemite, and perseite.

Note on the Formation of Aromatic Fatty Ketones by the aid of Chloride of Aluminium.—J. Boeseken.—The ordinary method of preparing the aromatic fatty ketones by the condensation of the aromatic hydrocarbides with the chlorides of the acids by the aid of chloride of aluminium gives but poor results; by taking care to use freshly prepared chloride of aluminium, *always in excess*, and not allowing the reaction to last too long, the author has succeeded in obtaining almost theoretical results. The product of the reaction is almost colourless, and the quantity of pure ketone obtained varies from 85 to 97 per cent of the carbide used.

On Camphor and its Derivatives.—G. Blanc.—A very long paper, not capable of useful abstraction.

On the Essence of Portugal.—J. Flatau and H. Labbé.—In the latest work on essence of Portugal (sweet oranges) myristic acid and myristicol have been found to be present. A new ether has also now been found; it has a very agreeable odour, very characteristic of oranges. It melts at 64° to 65°, and is easily soluble in ether, benzene, and chloroform in the cold, difficultly so in warm alcohol; it is almost insoluble in cold alcohol, light ligroin, and boiling water. In an etherised solution a large quantity of bromine is absorbed; after driving off the ether and washing with cold alcohol we obtain a pale yellowish powder, melting at 56° to 57°, easily soluble in ether, cold benzene, and chloroform, and insoluble in ligroin and boiling alcohol. Analysis shows the presence of a large quantity of bromine in the molecule of this new compound.

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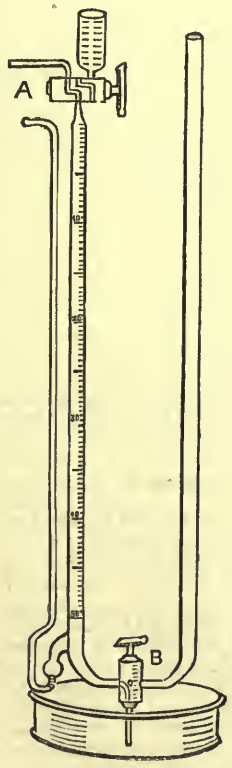
THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2022.

ON A MODIFIED FORM OF NITROMETER FOR USE IN NITROGEN ESTIMATIONS BY THE ABSOLUTE METHOD.

By H. A. D. JOWETT, D.Sc. and F. H. CARR, A.I.C.

During the progress of the investigation of the aconite alkaloids it was necessary to conduct a large number of determinations of nitrogen by the absolute method, and to examine chemically the gas so obtained (Jowett, *Trans. C. S.*., 1896, p. 1524; Dunstan and Carr, *Proc. C. S.*, 1896, p. 48).



For this purpose the special form of nitrometer to be described was designed. An extended experience with it has made manifest so many points in which it is superior, in our opinion, to other forms that it has been thought desirable to give a brief description of the apparatus.

The construction of the nitrometer is simple and the diagram hardly needs further explanation.

In using the apparatus the nozzle of the tap B is kept immersed in the potash solution contained in the dish, and the tap is turned so that the potash is expelled through this nozzle by the incoming gas.

When it is desired to read the volume of the gas, the liquid in the two columns is brought to the same level by use of the three-way tap B.

The advantages gained by the use of this nitrometer over other forms, when indiarubber tubing is not used, may be briefly summarised as follows:—

1. The gas may be readily washed by allowing potash solution to flow through the apparatus: this enables the measuring limb to be of small capacity, and capable of more accurate reading than is common with most nitrometers. In this case there is no fear of the potash solution becoming saturated with carbonic anhydride, and thus spoiling the combustion.

It has been our custom to keep a gentle stream of potash flowing during a combustion, re-filling the cup at intervals.

2. By working under considerably diminished pressure an even current of gas can more readily be maintained, and the risk of bursting the heated tube is lessened.
3. The gas may be drawn off for subsequent analysis.
4. It is usual in a combustion to first pass carbonic anhydride through the tube to drive out all the air, and the frequent testing of the gas to see if all the air is expelled necessitates — in the ordinary Schwarz's nitrometer—the filling and emptying of the potash in the side limb, an operation which is entirely avoided in the use of the nitrometer now described.

The apparatus is not much more expensive than the ordinary form of nitrometer, and could readily be obtained from any instrument maker.

ON THE SYNTHESIS OF ALBUMIN.

By ALFRED H. ALLEN.

The announcement of Dr. Leo Lilienfeld at the recent International Congress of Applied Chemistry at Vienna, that he had effected the synthesis of albumin, will be received by chemists with considerably more scepticism than it has met at the hands of the professional paragraphists. The circumstances of the announcement are not such as to encourage implicit faith in the reality of the alleged discovery, but Dr. Lilienfeld may be the victim in this respect of the professional zeal of the reporter.

From the accounts which have hitherto come to hand, it appears that it is not true albumin of which Dr. Lilienfeld claims to have effected the synthesis, but "peptone," which is a very different thing. It is said to be produced by the condensation of glycocine (amido-acetic acid) with phenol, by means of phosphorus oxychloride. The reaction is said to occur quantitatively and with great facility, allowing of the whole process being shown at the meeting. Further, Dr. Lilienfeld is said to have demonstrated, by the most conclusive tests, the absolute identity of his product with natural peptone, or—according to some accounts —with true albumin. Seeing how very ill-defined are the chemical tests for "peptone," and that more than one kind of peptone is recognised, this part of the account must be received with caution. Still more doubt attaches to the statement that Dr. Lilienfeld's product has the same elementary composition as natural peptone (or albumin). Seeing that natural albumin and peptone both contain sulphur as an essential constituent, and that Dr. Lilienfeld's process does not involve the employment of sulphur in any form, there seems to be a screw very loose somewhere.

Although the description of the mode of formation of Lilienfeld's body appears to negative the conclusion that he has effected the synthesis of either albumin or peptone, it by no means follows that he has not produced an albuminoid substance of great theoretical interest. He has undoubtedly been working in the right direction—in fact, his method may not improbably have been suggested by the interesting and ingenious suggestions of Dr. P. W. Latham (Croonian Lectures, 1886).

Commencing with the fact that by the reaction of hydrocyanic acid on aldehyd, cyan-ethylic alcohol,—

$$CH_3.CH(CN).OH,$$

is formed, Latham points out that the cyan-alcohols are, as a class, very unstable bodies, readily undergoing change, and when treated with ammonia form unstable cyan-amides, which easily undergo condensation with formation of imido-nitriles and elimination of ammonia. Latham thinks these facts suggest the enquiry :—"Have we not in these cyanogen compounds substances possessing some properties that belong to living tissue, namely, those of undergoing intra-molecular change and also condensation? And, further, if from these substances we can obtain the various products which result from the disintegration of albumin, may not albumin itself be simply a compound made up of these elements?"

In the laboratory, it is practicable to obtain from these cyan-alcohols the corresponding amido-acids, glycocine, leucine, &c.,* and all the acids of the acetic and lactic series. Latham suggests that, if it were found possible to reverse the process, albumin might be built up theoretically from such constituents.

Latham further instances the well-known molecular transposition by which ammonium cyanate is converted into urea, and quotes Pflüger's remark that the great molecular energy of cyanogen compounds suggests that the functional metabolism of protoplasm by which energy is set free may be compared to the conversion of the energetic unstable cyanogen compounds into the less energetic and more stable amides. In other words, that *ammonium cyanate* is a type of living, and *urea* of dead, nitrogen, and that the conversion of the former into the latter is an image of the essential change which takes place when a living proteid dies.

In accordance with this view, the group $-CO.NH-$ is dead nitrogen, and would, on becoming part of a living tissue, be transformed into $=C:N.OH$.

Cyanic acid, CNOH, is itself readily susceptible of polymerisation, with formation of cyamelide, $C_3H_3N_3O_3$.

Latham points out that the glycines are capable of uniting with each other, glycocine being not improbably glycocine amidoacetate,—

$$H_3N\left\{\begin{matrix}O.CO.CH_2\\CH_2.CO.O\end{matrix}\right\}NH_3;$$

and that by the dehydration of this and allied bodies, cyan alcohols might be formed.

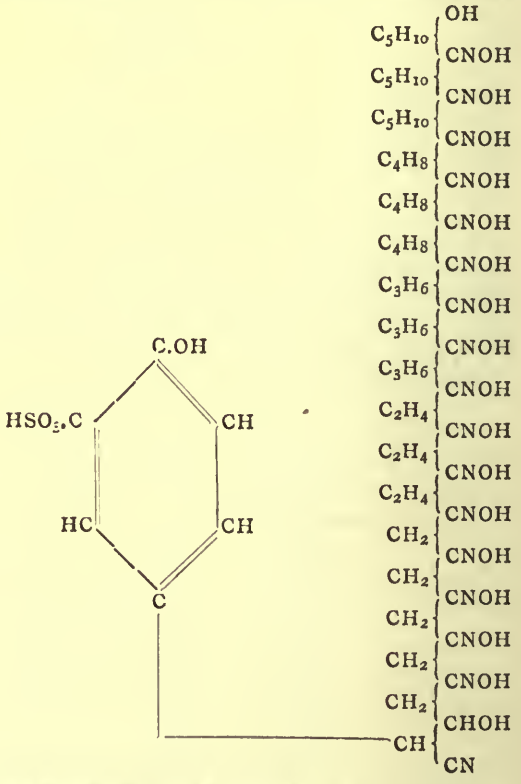
Thus, a double molecule of glycocine by dehydration would give a substance which might contain either a CO.NH group or a C:N.OH group, according to the arrangement of the atoms in the molecule.

$$2CH_2\left\{\begin{matrix}NH_2\\COOH\end{matrix}\right. - H_2O = \left\{\begin{matrix}CH_2\left\{\begin{matrix}NH_2\\CO\end{matrix}\right.\\CH_2\left\{\begin{matrix}NH\\COOH\end{matrix}\right.\end{matrix}\right. = \left\{\begin{matrix}CH_2\left\{\begin{matrix}NH_2\\C:N.OH\end{matrix}\right.\\CH_2\left\{\begin{matrix}\\COOH\end{matrix}\right.\end{matrix}\right.$$

Tyrosine is a member of the glycine group, and has the constitution of a para-hydroxyphenyl-amidopropionic acid. Latham shows that, by coalescence with glycocine and elimination of water, it would yield a body of the following constitution :—

$$C_6H_4(OH)-C_2H_3\left\{\begin{matrix}CH_2\left\{\begin{matrix}NH_2\\C:N.OH\end{matrix}\right.\\COOH\end{matrix}\right.$$

By similar ingenious reasoning, Latham shows how such a body as taurine may be introduced into the molecule, and he finally builds up the following formula as possibly representing the constitution of albumin :—



This suggestive formula contains $C_{72}H_{118}N_{18}O_{22}S$, and differs only by H_6 from Lieberkühn's formula for albumin, $C_{72}H_{112}N_{18}O_{22}S$.

The discovery of lysine, lysatine, and trypsophan or protein-chromogen, necessitates some modification of the above formula, which, of course, cannot be regarded as more than an ingenious and highly suggestive arrangement, which might be of service as a working hypothesis.

Pflüger has observed, and Loew and Bokorny corroborated the fact, that living proteid matter in the cells of various algæ reduces silver from a dilute alkaline solution of the nitrate, but that dead protoplasm or proteid does not give the reaction. Hence it is suggested that a compound of aldehydic nature exists in living protoplasm. By the reaction of formic aldehyd with ammonia, aspartic aldehyd may be supposed to be formed, a body which, though unknown, has the same composition as leucine. By its repeated polymerisation in presence of hydrogen and a sulphur compound, with elimination of water, the following equation may be realised :—

$$6C_{12}H_{17}N_3O_4 + H_2S + 6H_2 = C_{72}H_{112}N_{18}SO_{22} + 2H_2O.$$

Grimaux (*Compt. Rend.*, xciii., 771) has proposed to define proteids as "nitrogenised colloids, which by hydrolysis split up into amidated acids, carbon dioxide, and ammonia." On heating aspartic anhydride to 130° with urea for two hours, Grimaux obtained a thick mass, completely soluble in boiling water to a gummy, highly colloid liquid, yielding highly gelatinous precipitates with acids, alkaline salts, magnesium and aluminium sulphates, solutions of iron, copper, and mercury, and with tannin. The jelly yielded by acetic acid dried up to a substance resembling dried albumin. It softened in boiling water without undergoing solution, but dissolved in caustic potash to a liquid giving a violet colouration with cupric sulphate.

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* $C_4H_9.CHO + HCN = C_4H_9.CH\left\{\begin{matrix}CN\\OH\end{matrix}\right.$
Valeric aldehyd. Pentyl cyan-alcohol.

$C_4H_9.CH\left\{\begin{matrix}CN\\OH\end{matrix}\right. + NH_3 = C_4H_9.CH\left\{\begin{matrix}CN\\NH_2\end{matrix}\right. + H_2O$
Pentyl cyan-alcohol. Pentyl cyan-amide.

$C_4H_9.CH\left\{\begin{matrix}CN\\NH_2\end{matrix}\right. + 2H_2O = C_4H_9.CH\left\{\begin{matrix}COOH\\NH_2\end{matrix}\right. + NH_3$
Pentyl cyan-amide. Leucine.

Of course it by no means follows, as Dr. Lilienfeld is reported to have said, that a synthetical product of the same ultimate composition as peptone will have the same food-value. This fact is familiar to the mere tyro; but it may be of interest to recall the case of quinine, the synthesis of which may any day be effected. Already two distinct basic substances isomeric with quinine have been prepared synthetically, but neither base has the physiological characters of true quinine.

Sheffield, August 13, 1898.

SIXTEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its Sixteenth Annual Report, covering the twelve months ending August, 1898.

Works Published.

"A Bibliography of the Metals of the Platinum Group," —Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium, 1748—1896. By Jas. Lewis Howe, Smithsonian Miscellaneous Collections, 1084. City of Washington, 1897. Pp. 318, 8vo.

This fine volume forms one of the most valuable and comprehensive indexes to an important field of chemical literature produced under the auspices of the Committee since its appointment in 1882. It shows on every page evidence of conscientious and critical skill; the author- and subject-indexes, with which the book concludes, are important features. Its workmanship and the method of presentation of data in type make Dr. Howe's volume a model.

"References to the Literature of the Sugar-Beet," exclusive of works in foreign languages. By Claribel Ruth Barnett. U.S. Department of Agriculture. Library Bulletin, June, 1897. 9 pp. 4to.

This carefully edited contribution to the bibliography of a subject interesting to the chemist as well as to the scientific farmer, manifests the activity of the U.S. Department of Agriculture in its Library.

"A Chemical Bibliography of Morphine, 1875—1896." By H. E. Brown, under the direction of A. B. Prescott. Completed in "Pharmaceutical Archives," vol. i., No. 3.

A supplement carries the literature through 1897. The separates contain an index of authors.

"A Bibliography of the Metallography of Iron and Steel." By Albert Ladd Colby. Published in the *Metallographist*, vol. i., No. 2, pp. 168—178, April. 1898.

This includes 188 titles, arranged alphabetically by authors, and numbered chronologically; it is reprinted, extended, and re-arranged from *The Iron Age*, Jan. 27, 1898, by the author.

"Review and Bibliography of the Metallic Carbides." By J. A. Mathews. *Smithsonian Miscellaneous Collections*, No. 1090. City of Washington, 1898. Pp. 32, 8vo.

Published by the Smithsonian Institution on recommendation of this Committee. Under each metal forming a carbide the author has given a brief synopsis of the chemical data with references to the literature on that subject. There is an author-index.

"A Catalogue of Scientific and Technical Periodicals, 1665—1895, together with Chronological Tables and a Library Check-List." By Henry Carrington Bolton. Second edition. *Smithsonian Miscellaneous Collections*, No. 1076. City of Washington. 1897. Pp. 1247. 8vo.

This bibliography was first issued in 1885, and the second edition has been prepared at the request of the Smithsonian Institution. It embraces periodicals in every department of pure and applied science, including of course chemistry and chemical technology. The Chronological Tables give the date of publication of each volume of about 550 periodicals; they enable one to ascertain the date of a given volume in a given series of a given work, or to determine the number of a volume when the date only is given. The Library Check-List shows in what American Libraries, 133 in number, complete sets of the periodicals may be found. The second edition brings the date down to 1895; its publication has been delayed by the compilation of the Check-List. The periodicals catalogued number 8603.

"Alkaloidal Estimation;" a bibliographical index of chemical research prepared from original literature for the Committee of Revision and Publication of the Pharmacopœia of the United States of America, 1890—1900, by Paul I. Murrill under the direction of Albert B. Prescott. Ann Arbor, 1898.

A pamphlet of about sixty pages, not for sale.

"The Review of American Chemical Research," edited by Arthur A. Noyes and published in the *Journal of the American Chemical Society*, completed vol. iii., in December, 1897. Two indexes, an author- and a subject-index, increase its value.

Mr. E. W. Allen, Acting Director of the Office of Experiment Stations, U.S. Department of Agriculture, in reply to inquiries, sends the following communication:—

"During the past year we have completed volume ix. of the 'Experiment Station Record' (1897—'98). This, like former volumes, contains abstracts of and references to articles on the methods and results of work in agricultural chemistry published in this country and in Europe. During the past year the review of Russian scientific periodicals has been added. About 2000 cards of the Card Index of Experiment Station Literature have been issued during the past year, making a total of 16,000 cards in this index at present. In addition to several accounts of chemical studies of the nutrition of man, the Office has issued a 'Report of Preliminary Investigations on the Metabolism of Nitrogen and Carbon in the Human Organism with a Respiration Calorimeter of Special Construction,' by W. O. Atwater, C. D. Woods, and F. C. Benedict, the work being carried on in part by funds furnished by this Office. In this connection may also be mentioned a compilation of over 400 pages of metabolism experiments in which the balance of income and outgo was determined, made by W. O. Atwater and C. F. Langworthy, and issued from this Office. The bulletin is a digest of about 3600 experiments with man and animals, in which the balance of one or more of the factors of income and outgo was determined. While this work may at first thought seem somewhat a field, it is chemical in its character as well as physiological, and has involved in some cases quite extensive chemical studies."

The "Digest of Metabolism Experiments" herein named forms Bulletin No. 45 of the Office of Experiment Stations, and constitutes a comprehensive bibliography of the subject.

The Committee chronicles the publication of the following bibliographies bearing more or less on chemical researches:—

"Contributions to the Bibliography of Gold." By A. Liversidge. Australasian Association for the Advancement of Science. Brisbane, 1895, 8vo.

"Analyst" (The). The organ of the Society of Public Analysts. General Index to the *Proceedings of the Society of Public Analysts*, vol. i. (1876), and to the

* From Advance sheets of the *Proceedings of the American Association for the Advancement of Science*, August meeting, Boston, 1898. Communicated by H. Carrington Bolton.

Analyst, vols. i.—xx. (1877—1896). Compiled by J. Cuthbert Welch. London, 1897. Pp. i.—181, 8vo.

Arranged on the dictionary plan, authors, subjects, and cross-references in a single alphabet.

"Bibliographie des Travaux Scientifiques" (Sciences Mathématiques, Physiques, et Naturelles), publiés par les Sociétés Savantes de la France. Par J. Deniker. Tome 1, part 2. Paris, 1897, 4to.

Part 1 was published in 1895. Most important for original papers published in France.

"Biographisch - Literarisches Handwörterbuch zur Geschichte der exacten Wissenschaften," von J. C. Poggendorff. Dritter Band (die Jahre 1858 bis 1883 umfassend). Herausgegeben von B. W. Feddersen und A. J. von Oettingen. Leipzig, 1897—98. Roy. 8vo.

This valuable addition to Poggendorff's well-known biographical dictionary is useful to chemists, inasmuch as it gives the titles of original papers by the principal chemists of the world published during the period specified.

Works in Preparation and Reports of Progress.

"A Subject- and Author-Index to the first twenty volumes of the *Journal of the American Chemical Society*" is being compiled by Mr. Sohon, who expects to complete the MS. in December, 1898.

"A First Supplement to the Select Bibliography of Chemistry, 1492—1897," by Henry Carrington Bolton, is now going through the press. It will form a volume of the *Smithsonian Miscellaneous Collections* of about 600 pages.

"A Second Supplement" to the same Bibliography, to contain chemical dissertations only, is well advanced, about 8000 titles being already in hand.

Dr. A. C. Langmuir reports the completion of his MS. "Index to the Literature of Zirconium."

Dr. C. H. Joüet reports the near completion of his "Index to the Literature of Thorium."

Mr. George Wagner reports progress on a "Bibliography of Oxygen."

The manuscript of an "Index to the Literature of Thallium, 1861—1896," by Miss Martha Doan, lately of Cornell University, was submitted to the Committee, through Prof. L. M. Dennis, and after critical examination it has been unanimously recommended to the Smithsonian Institution for publication.

Dr. Alfred Tuckerman is engaged upon new editions of his "Indexes to the Literature of the Spectroscope, and of Thermodynamics," which are to be continued to the year 1900. He also reports progress on the "Index to the Mineral Waters of the World," the printing of which has been delayed by mechanical difficulties.

Dr. Willem P. Jorissen, of Rotterdam, has undertaken to bring down to date Prof. Albert R. Leeds' "Indexes to Ozone and to Hydrogen Peroxide," first issued in 1880, and long since out of print.

Monsieur Jules Garçon, chemical engineer (of 40 *bis* Rue Fabert, Paris), is about to publish an important contribution to the bibliography of technical chemistry, entitled "Répertoire Universel de Bibliographie des Industries Tinctoriales et des Industries Annexes." It is expected to form three large volumes. In the preparation of this immense undertaking the author has examined 1800 works and 111 sets of periodicals, the latter in 5000 volumes, besides 7000 other articles and documents. Subscriptions (100 francs) may be sent to the publishers, Gauthier-Villars et fils, Paris. M. Garçon is known as the author of the "Bibliographie de la Technologie Chimiques des Fibres Textiles," Paris, 1893, noted in our Thirteenth Annal Report.

Two unfinished manuscript indexes are at the disposal of persons willing to undertake their completion:—An "Index to the Literature of Carbonic Oxide," begun by the late Prof. William Ripley Nichols and continued by Prof. Augustus H. Gill; and an "Index to the Literature of Milk," begun by Prof. Clement W. Andrews.

As stated in previous reports, this Committee does not attempt to prescribe a fixed plan for volunteer indexers, but leaves method and topic to be chosen by compilers; the Committee does not seek to control the productions further than to insure work of high merit and to guard the interests of the Smithsonian Institution, which has agreed to publish manuscripts endorsed by the Committee. Chemists willing to undertake the compilation of indexes are requested to send their names and addresses, with a memorandum of the subject chosen, to the Chairman of the Committee (Cosmos Club, Washington, D. C.), who will furnish sample copies of indexes and other information.

Committee:—

H. CARRINGTON BOLTON, Chairman,
F. W. CLARKE,
A. R. LEEDS,
A. B. PRESCOTT,
ALFRED TUCKERMAN,
H. W. WILEY.

ESTIMATION OF TIN IN SALTS OF TIN.

By MM. A. FROENKEL and J. FASAL.

THE authors have planned out a method for the estimation of tin which consists in precipitating this metal on aluminium, dissolving the two metals in hydrochloric acid, and titrating the stannous chloride thus formed by means of iodine or bichromate of potassium. But in this case it is indispensable to first of all neutralise nearly the whole of the hydrochloric acid. The method is as follows:—

The solution of the salt of tin containing 0·2 to 0·4 grms. of the metal is placed in a flask and a few drops of hydrochloric acid added, then from 0·5 to 1·0 grm. of aluminium wire. This is gently heated, and the tin is precipitated after about half an hour. At the end of this time 10 cubic centimetres of concentrated hydrochloric acid are added, and the whole warmed until the complete solution of both the metals has taken place; this requires about fifteen minutes. Bicarbonate of soda and Seignette's salt are added until the reaction is alkaline. It is then titrated with iodine.

This method, tried with a solution (A) containing 0·4317 grms. of tin, and on another solution (B) containing 0·3988 grms of tin, gave the following results—

		A.	B.
1.	Tin found	0·4105	0·3866
2.	„	0·4105	0·3875
3.	„	0·4038	—

To find the difference between the quantity of tin actually existing in the solution and that found by analysis, we dissolved 2·8302 grms. of pure tin in hydrochloric acid, traversed by a current of carbonic acid. The volume of the solution was made up to 250 cubic centimetres, and 25 cubic centimetres of this solution were titrated in the manner already described. Another portion of 25 cubic centimetres was taken and oxidised, then precipitated either by sulphate of soda or by nitrate of ammonia; the oxide of tin was then weighed.

The following are the comparative results :—

Titration by iodine (1)	0·2765 grm.
,, ,, (2)	0·2767 ,,
Titration by bichromate of potash	0·2736 ,,
Precipitation by sulphate of soda..	0·2870 ,,
Precipitation by nitrate of ammonia	0·2844 ,,

The theoretical result should be 0·2830 grm. of metallic tin.

The method is therefore a sufficient approximation for commercial purposes, and more especially in comparative analyses.—*Mitt. d. K. K. Tech. Gewerbe Museums in Wien*, vol. vii., p. 227.

ON THE ESTIMATION OF LEAD AND ANTIMONY IN TIN-FOIL.

By A. SEYDA.

Estimation of the Lead.—Ten grms. of the foil are dissolved in hydrochloric acid at 25 per cent, and a solution of nitric acid also at 25 per cent is added for the purpose of transforming the stannous chloride into stannic chloride, and to dissolve the antimony which remains unattacked by the hydrochloric acid. Drop by drop a solution of caustic soda at 25 per cent is added until the precipitate formed becomes re-dissolved. By maintaining the temperature at a point near boiling there is generally nothing but a slight opalescence left. We then add a small quantity of precipitated sulphur and treat with a current of sulphuretted hydrogen until the liquid takes a decidedly yellow tint. It is then allowed to stand for twenty-four hours, when the black precipitate is filtered off, washed with a solution of sulphide of sodium until a small portion of this clear liquid, acidulated with hydrochloric acid, gives a decidedly white deposit of sulphur. This washing requires a considerable time, but it is indispensable if we require the complete removal of the tin. The filter containing the moist precipitate is gently heated with nitric acid at 25 per cent, the solution is filtered, and the exhaustion with nitric acid repeated until a small portion of the filtered liquid no longer gives a black precipitate with sulphurretted hydrogen.

The nitric solution containing all the lead is evaporated down with 20 cubic centimetres of sulphuric acid. The sulphate of lead is filtered and weighed in the usual manner.

Estimation of the Antimony.—Five grms. of the tin-foil are thrown, a little at a time, into a mixture of 100 cubic centimetres of concentrated nitric acid and 25 cubic centimetres of water. The metastannic acid is treated with nitric acid at 25 per cent in a porcelain crucible and the mixture evaporated to dryness. The residue is dried on the water-bath. It is essential that the temperature of desiccation should not exceed 100° C., for the anhydrides of the oxides of tin and antimony do not appear to combine with soda. The still warm powder is thrown a little at a time into 60 grms. of caustic soda in a state of fusion. The melted mass is cooled to about 100°, broken up, and dissolved in 700 cubic centimetres of water. The cloudy liquid is cooled, and one-third of its volume of alcohol at 95 per cent is added, and the whole left for twenty-four hours. The precipitate is filtered by decantation, and the last portions washed on to a filter by means of a mixture of 1 part of water to 2 parts of alcohol. Instead of washing the precipitate with dilute alcohol, an operation which always removes a small portion of the antimony, it is better to repeat the fusion with caustic soda a second time. The precipitate is dried at 100° and separated from the filter. The latter is cut up into strips and thrown into 10 grms. of melted caustic soda containing a small quantity of nitrate of soda. When the paper is entirely consumed we add the precipitate and proceed as before.

To make quite sure of the insolubility of the antimoniate of soda, the liquid should contain about 10 per cent of caustic soda and 25 per cent of alcohol. The antimony is finally precipitated in the state of sulphide.—*Zeit. fur Offent. Chem.*, vol. iii., p. 364.

ON THE ELECTROLYTIC SEPARATION OF SILVER AND COPPER.

By N. REVAY.

These two metals may be separated one from the other by means of electrolysis, the silver salts requiring a slightly lower difference of potential than the corresponding salts of copper. The electrolysis can be effected either in acid solution or in a solution of double cyanides.

A. *Electrolytic Precipitation of Silver in Acid Solution.*—In the first experiment the electromotive force used was 1·3 to 1·4 volts. The silver was deposited in the spongy state; but this inconvenience can be avoided by heating the electrolyte to a temperature of 70° C.; the deposit of silver is even then not quite homogeneous, nevertheless it can be washed and weighed in this state. The electromotive force should not exceed 1·4 volt. To prevent the formation of peroxide, the solution should be kept strongly acid with nitric acid from the commencement of the reaction. The author has carried out experiments on solutions containing 0·25 to 0·50 grm. of nitrate of silver, and practically equal quantities of crystallised sulphate of copper. Four separate analyses showed that the nitrate of silver used contained 63·43, 63·47, 63·45, and 63·35 per cent of silver. These results may be looked upon as being very accurate.

B. *Electrolytic Precipitation in a Cyanide Solution.*—The separation based on this method was first suggested by Smith and Frankel. It was also experimented upon by Heydenrich and Frendenberg. In this case it is much more difficult to get a determined and constant electromotive force, as the difference of potential between the silver electrode and the solution varies considerably with the concentration of the silver salt and the proportion of cyanide of potassium in solution. According to Frendenberg the precipitation of the silver commences at 1·7 to 1·8 volts, while the copper is not deposited with an electromotive force lower than 2·3 to 2·4 volts; according to the present author, these last figures are a little too high. Experiments were made with an electromotive force of 1·6 to 1·8 volts at a temperature between 45° and 60°; the results obtained were very satisfactory. For six determinations made on electrolytes containing from 0·23 to 1·63 grms. of nitrate of silver he obtained 63·37 to 63·45 per cent of silver present in the salt used.

This method is preferable to the first one, inasmuch as it gives a more coherent metallic deposit. It gives better results still when the proportion of silver is high as compared with that of the copper present. On the other hand it is much less exact than the other method—to such an extent in fact, that if the copper is present in great excess it is precipitated the first.—*Zeitschrift fur Elecktrochemie*, vol. iv., p. 313, 1898.

THE ACTION OF SULPHUR UPON METALLIC SODIUM.

By JAMES LOCKE and ALFRED AUSTELL.

Among the various investigations which have been published regarding the action of sulphur upon metallic sodium but one is of recent date. Rosenfeld (*Ber. d. Chem. Ges.*, vol. xxiv., 1658), in a short article relating to the reactions of sodium, confirms the observations of Davy, Gay-Lussac, and Thenard, that the two combine with nearly explosive force, even at the ordinary tempera-

ture. Rosenfeld seems to have made no analysis of his reaction-products, but says that by mixing finely divided sodium, sulphur, and sodium chloride together, and rubbing, he obtained a violent reaction, in which a mixture of the monosulphide and polysulphides was formed. His work is accordingly given in the various reference books as indicating a method for preparing sodium monosulphide.

Through a chance observation made while preparing sodium sulphide in some other work, we have been led to study this reaction more closely. As it is practically impossible to separate the products from any sodium which may have been left unaltered in the reaction, a quantitative investigation of their composition is extremely difficult, and our results are therefore only approximate. They indicate conclusively, however, that the monosulphide cannot be formed by the direct combination of sodium and sulphur at temperatures below 220°.

Our method of procedure was as follows: A small weighed quantity of clean sodium was covered with about 50 c.c. of dry toluene, and the latter heated until the sodium fused. This was carried out in a small flask fitted with a return-condenser and a separatory-funnel. Through the latter the calculated quantity of sulphur, dissolved in hot toluene, was slowly added, while the contents of the flask were kept briskly boiling. The reaction at first results only in a thin yellow film of polysulphide* being formed upon the surface of the sodium. It soon grows violent, however; the sodium swells up, and a porous cake of the compound is formed. After this main reaction, which lasts but a few seconds, has subsided, the rest of the sulphur solution was added rapidly, and the mixture boiled for about an hour. The product was then filtered, washed with hot toluene, dried, and tested for sodium. The presence of uncombined sulphur in the mother-liquid could readily be seen from the yellow colour of the latter. When no free sodium was found, the substance was submitted to analysis.

Experiments were made successively with 2 grms. of sodium and the quantities of sulphur calculated for the compounds Na_2S, Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5. The results are tabulated below:—

Ratios. Na : S.	Sodium. Grms.	Sulphur. Grms.	Product.	Filtrate.
2 : 1	2·0	1·39	Yellow, mixed with much Na	Colourless
2 : 2	,,	2·78	,,	,,
2 : 3	,,	4·17	Traces of Na	,,
2 : 4	,,	5·56	No Na	Yellow
2 : 5	,,	6·95	,,	,,

According to these results the only compound formed at 110°, the boiling-point of toluene, should approximate rather closely to the formula Na_2S_3. That no lower sulphide is formed is clear, and at this temperature metallic sodium has apparently no action upon the polysulphides. In the first two experiments, as the toluene cooled down, the globules of sodium left showed in fact a bright metallic lustre. The products of the last two experiments, in which there was no residual sodium, were analysed by conversion into the sulphate. They had practically the same composition with 28·89 and 28·57 per cent sodium respectively. The percentage of sodium calculated for the compound Na_2S_3 is 32·32, and for Na_2S_4 26·44. Both products were therefore probably mixtures of these two compounds. That more or less of the higher sulphide is formed is also indicated by the fact that the product obtained in the third experiment (Na : S = 2 : 3) contained a small quantity of free sodium.

An experiment was also made in which naphthalene was substituted for toluene, a temperature of 218° being thus obtained. It seemed probable that at this heat a compound containing less sulphur would be formed, if only by the action of sodium upon the polysulphides after the first reaction had taken place. This turned out, however, not to be the case. 2·78 grms. sulphur were dissolved in toluene, and added to 2 grms. sodium under hot naphthalene. The small quantity of toluene was then distilled off, and the naphthalene kept boiling for an hour. The product contained apparently as much free sodium as that obtained with a mixture of the same proportions at 110°.—*American Chemical Journal*, xx., No 7.

* The fact that the film is yellow shows that even when a great excess of sodium is present no monosulphide forms, as the latter has a red colour. In every experiment made, a greenish-yellow product was obtained.

THE

CONDUCTIVITY OF AQUEOUS SOLUTIONS OF PRASEODYMIUM AND OF NEODYMIUM SULPHATES.

By H. C. JONES and H. M. REESE.

The salts used in this work were those which had been employed by one of us (*Am. Chem. Journ.*, xx., 345), in determining the atomic weights of praseodymium and of neodymium. The partly purified compounds were kindly furnished by Mr. Waldron Shapleigh. These were further purified by the method described in the article already cited, and, as there shown, the amount of impurities which remained in the compounds must have been small.

The solutions of the sulphates, which had been made from the oxides, in determining the atomic weights of the metals, were evaporated to dryness, and heated above the boiling-point of sulphuric acid, until constant weight was attained. The salts was then allowed to cool, in weighing-tubes with ground-glass stoppers, and from these sulphates the following solutions were prepared.

The water used had been purified from ordinary distilled water, by the method described by Jones and Mackay (*Ibid.*, xix., 91), and was found to have an inappreciable conductivity.

In order to avoid the accumulative error which results from diluting a solution a large number of times, this was not repeated very often. A part of the original solution was diluted three or four times in succession, by removing a known volume from it, and adding a measured volume of water. The next dilution was prepared directly from the original solution, in a measuring-flask. This solution was then used as the starting-point in making the following three or four dilutions. The next more dilute solution was made directly from the original solution, and so on.

The Kohlrausch conductivity method, with Ostwald thermostat, was employed, and the cell standarised as usual with N/50 potassium chloride, which had been very carefully purified.

A solution of praseodymium sulphate was prepared containing 7·737 grms. in 200 c.c., which was equivalent to 38·685 grms. to the litre. The molecular weight of praseodymium sulphate was taken as 569·1; hence the above solution was 0·06798 normal, or its volume was 14·71. From this solution all the more dilute solutions of this salt were prepared as already described.

The solution of neodymium sulphate which was prepared contained 11·3595 grms. in 500 c.c. or 22·7190 grms. in a litre. The molecular weight of neodymium sulphate was taken as 575·4, the volume of the above solution being then 25·326. From this all the more dilute solutions were made.

The dilutions used, and the molecular conductivities found, for both salts, are given in the following table. v is the volume, or the number of litres which contains a grm.-molecular weight of the salt, and μ_v the molecular conductivities.

	Praseodymium sulphate.		Neodymium sulphate.	
	v.	μv.	*v.*	μv.
1	14·71	98·33	25·33	115·03
2	29·42	117·43	50·65	137·65
3	58·84	141·42	101·31	166·35
4	117·68	169·47	202·61	197·91
5	294·2	217 83	506·5	255·43
6	588·4	262·65	1013·0	303·45
7	1176·8	317·10	2026·0	366·0
8	1471·0	331·43	2532 6	382·9
9	2942·0	403·37	5065·2	462·5
10	5884·0	482·61		

—*American Chemical Journal*, xx., No. 7.

THE ATOMIC WEIGHT OF CADMIUM.*

By H. N. MORSE and H. B. ARBUCKLE.

HAVING re-determined the atomic weight of zinc (*Amer. Chem. Journ.*, xx., 195) by the method of Morse and Burton (*Ibid.*, x., 311), making corrections for the gas which Richards and Rogers (*Proc. Am. Acad.*, xxviii.,200) found to be retained by the oxide, even at high temperatures, we undertook a similar repetition of the work of Morse and Jones (*Amer. Chem. Journ.*, xiv., 261) on the atomic weight of cadmium, for the purpose of correcting their results, if cadmium oxide should also be found to retain gas.

Richards and Rogers found no gas in their specimens of cadmium oxide, but as their material had been heated to a higher temperature than is permissible in an atomic weight determination of this metal, we could not be certain that the oxide of Morse and Jones was likewise free from gas. Moreover, it was found by Bucher ("Dissertation," 1894, p. 22), in this laboratory, that when a given weight of cadmium oxide, derived from the carbonate, is converted into nitrate, and then again into oxide, the last weight of the oxide is greater than the first. The experience of Bucher points directly to the presence of gas in the oxide from the nitrate.

Another sufficient reason for a revision of the work is to be found in the fact that the results which have been obtained by work upon the halogen salts of cadmium have been throughout notably higher than those based on the weight of the oxide. It appeared desirable to clear up, if possible, the cause of this discrepancy between the two methods.

The metal which was used in this work was the same as that employed by Morse and Jones. It was, in fact, a portion of that prepared for the earlier experiments. It had been purified by six fractional re-distillations in a vacuum, and examined spectroscopically by Professor Rowland. The details of the distillation process have already been described (*Amer. Chem. Journ.*, x., 311, and xiv., 261) need not be repeated.

The nitric acid with which the metal was dissolved was prepared, as in the earlier work upon zinc and cadmium, by condensing the vapours of the acid upon the surface of a large platinum dish: 15 c.c. portions of it, when evaporated in platinum, gave no visible or weighable residue. We deemed it necessary to test the latter condition with unusual care, because of the wide difference between the atomic weights of cadmium and oxygen, and the correspondingly large effect of small errors in weight of material upon the results.

The arrangement of the crucibles in which the metal was converted first into nitrate, then into oxide, and finally weighed, was the same as that formerly used for both cadmium and zinc. It consisted of a small porcelain crucible (No. oo) in which the metal was dissolved, and a larger one (No. II.) in which the smaller one was placed. The smaller, but not the larger, crucible was provided with a lid. The lid and the crucible were, however, separated by means of bent pieces of platinum wire hung over the edge of the latter, thus providing for the free escape of vapours during the solution of the metal and the conversion of the nitrate into the oxide. The glaze was removed from the bottoms of the crucibles, also from the underside of the lid, by means of hydrofluoric acid. The pair of crucibles was weighed together and never separated. A similar, but slightly lighter, pair of crucibles was prepared at the same time to serve as a counterpoise. The platinum hooks belonging to the two sets were brought to nearly equal weight by filing, and then fragments of porcelain were added to the counterpoise until the weights of the two pairs differed by only a small fraction of a m.grm. Both were then heated under the same conditions for several hours. The difference between their weights was then carefully determined, after which they were again heated, in order to determine whether the difference remained constant. Throughout the entire determination the two sets of crucibles were treated as nearly alike as the purposes for which they were used would permit; for instance, if the pair in which the metal had been dissolved was heated, the tare was heated under the same conditions for the same length of time.

Owing to the volatility of cadmium oxide at high temperatures, it was necessary to give careful attention to our heating arrangements. A small double-walled furnace was made of asbestos board. Two opposite sides were cut away near their centres to permit the entrance of blast-flames, and the upper edges were notched to allow the products of combustion to escape. The bath, in which the crucibles previously described were heated, consisted of a large porcelain crucible. This was inserted in a hole in the piece of asbestos board which served as a cover to the furnace. In the bottom of the bath was placed a piece of unglazed porcelain on which the crucibles rested while being heated.

For the air-blast we had a small Root blower which was run by an electric motor; and, as the current was very constant, we were able to maintain quite uniform temperatures. The lamps which we first tried were two glass-blower's lamps with two jets each. These, with a given adjustment of air and gas-cocks, and speed of the blower, gave us a temperature in the furnace which lay between the fusing-points of sodium chloride (776°) and potassium carbonate (835°). As the former salt fused very readily, while the latter showed no signs of having been softened, we judge that the temperature must have been about 800°. At this temperature it was found practicable to reduce the oxide to constant weight. To ascertain whether a higher temperature might not be employed with safety, we substituted ordinary blast lamps for those first selected. These gave us a temperature between the fusing points of pure silver (960°) and potassium sulphate (1066°). But it was found that, at this temperature, specimens of oxide which had been brought to constant weight under the first arrangement began to lose in weight. That the loss was due, in part at least, to sublimation was clear from the fact that portions of the crucible previously white became tarnished with a yellow coating. The blast-lamps were therefore exchanged for those we had used in the first place, and no further change of lamps, or of gas or blast adjustments, was made during the entire work. The temperature was, however, tested from time to time, but always with the same result; sodium chloride fused readily, while potassium carbonate remained unfused, after heating for an entire day.

The apparatus for the liberation, collection, and analysis of the occluded gases was that devised for our earlier work on the atomic weight of zinc (*Amer. Chem. Journ.*, xx., 196). The manipulation of the specimens of oxide and of the gases was also the same as on the former occasion. We stated in our account of the work upon zinc that, in our judgment, the necessary errors connected

* The work of which an account is given in this article was carried out under a grant from the Bache Fund (National Academy of Sciences).

with the gas analytical part of the determinations coulde not exceed 1 per cent of the correction. To test th reasonableness of this estimate, we made determinations of oxygen in three specimens of air whose volumes varied between 0·4 and 0·5 c.c. The percentages of oxygen found were 20·79, 20·98, and 20·80.

According to C. Langer and V. Meyer (*Pyrochemische Untersuchungen*, Seite 66) nitric oxide is not at all dissociated at temperatures between 900° and 1200°. Emich (*Monatshefte fur Chemie*, xiii., 615), on the other hand, states that the dissociation begins at 700°, is small at 900°, is only two-thirds completed at 1200°, and is not finished until the fusing temperature of platinum is reached. The results of both investigations indicate that the temperature of initial dissociation is higher, and its progress slower, than had hitherto been supposed. In view of the fact, therefore, that our oxide was never heated much above 800°, we had to fear the presence in it of oxides of nitrogen, a condition which would have increased very greatly the difficulty of the problem in hand. The following method of testing for the presence of nitric oxide, or other oxides of nitrogen, was adopted:—A wide-mouthed salt bottle was moistened on the inside with water; a crucible containing a quantity of cadmium oxide which had been heated to constant weight was introduced; a small quantity of dilute sulphuric acid, free from nitric acid, was added to the oxide, and the bottle closed. After standing for several hours, the liquid within was tested for nitric acid by the brucine reaction. None was found. In the subsequent work, the acid in which a specimen of oxide had been dissolved was examined, in every case, by means of the brucine reaction. In no instance, however, was any evidence of the presence of nitric acid found. In view of the fact that about 20 per cent of the gas retained by the oxide proved to be free oxygen, we judged that an examination of the solution, in the manner indicated, was sufficient to demonstrate the presence or absence of nitric oxide or other oxides of nitrogen.

Having converted the dried nitrate into a uniformly dark brown mass, at low temperature, the crucibles were placed in the furnace, previously described, and heated for a period of five or six hours. The tare was then heated for the same length of time, and the weight of the oxide determined. This operation was repeated, without variation, from five to eight times, until no change in the weight of the oxide could be detected after three successive heatings. The crucibles containing the oxide were then brought into our apparatus for dealing with the occluded gases, and there the oxide was treated in the same manner as the oxide of zinc in our earlier work (*Amer. Chem. Journ.*, xx., 195).

When the oxide of zinc is dissolved in dilute sulphuric acid, the evolution of the gas is slow, and continues as long as any of the material remains undissolved. In the case of the oxide of cadmium, on the other hand, a very different phenomenon presents itself. The instant the dilute acid strikes the oxide in the vacuum, there is an almost explosive evolution of gas; and though the solution of the oxide requires some time, but little gas is obtained after the instant of first contact between acid and oxide. The water vapour in the space above the crucibles condenses to a visible mist which settles upon the interior glass surfaces. The disturbance in the oxide, during this sudden liberation of gas, is so great that we were obliged to take measures to prevent it from being thrown out of the crucibles. The gas was collected and analysed in precisely the same manner as that obtained from the oxide of zinc.

The results of the nine determinations which were made are presented in the accompanying Table.

The uncorrected result, 112·084, is very close to the value 112·071 (112·06 with all corrections applied to weighings) which was obtained by Morse and Jones (*Amer. Chem. Journ.*, xiv., 264); while the corrected result, 112,377, accords equally well with the mean values

	Weight of cadmium.	Weight of oxide.	Uncorrected atomic weight.	Volume of gas (st. cond.). C.c.	P.cent. of oxygen.	Corrected atomic weight.
1	1·93188	2·20764	112·092	0·574	21·25	112·392
2	1·67935	1·91910	112·074	0·480	25·16	112·365
3	1·48430	1·69620	112·076	0·441	19·95	112·376
4	1·36486	1·55972	112·071	0·402	18·33	112·368
5	1·50295	1·71744	112·112	0·419	21·95	112·394
6	1·43804	1·64330	112·093	0·431	18·56	112·395
7	1·44041	1·64604	112·079	0·406	20·93	112·365
8	1·45938	1·66771	112·082	0·421	21·85	112·375
9	1·40379	1·60420	112·076	0·390	19·50	112·359
			Mean = 112·084			Mean = 112·377

112·39 and 112·38, which were obtained by Bucher ("Dissertation," pp. 11 to 18), in his work upon the chloride and bromide of cadmium.

The relation of the volume of the occluded gas to the weight of the oxide is remarkably constant, as will be seen from the following Table, in which is given for the individual determinations the volume of gas per grm. of oxide:—

	C.c.		C.c.		C.c.
1	0·260	4	0·258	7	0·246
2	0·250	5	0·244	8	0·252
3	0·260	6	0·262	9	0·243

The mean volume of the gas per grm. of the oxide is 0·253 c.c. as against 0·301 for the oxide of zinc.

A few experiments were made in order to determine whether the gas could be extracted without dissolving the oxide. The first of these was to ascertain whether the oxide, under water, would lose any portion of its gas when left for a long time in a vacuum. The bulb containing the acid was emptied and thoroughly washed with pure water, and then filled with water of perfectly neutral reaction. The water in the bulb was exhausted by occasional pumping until no trace of air could be obtained from it. A specimen of the oxide which had been heated for the usual length of time was then brought into the apparatus and covered with water. After exhausting again as completely as possible, connection with the pump was cut off and the oxide allowed to stand undisturbed for three days in the vacuum. Not a trace of gas was liberated. The next experiment was to determine whether boiling water would liberate the gas. A specimen of the oxide, weighing 1·4134 grms., which had been heated the usual length of time, but not tested as to the constancy of its weight, was heated for six hours under boilng water, and then dissolved in a vacuum. The volume of gas obtained was 0·403 c.c., or 0·284 c.c. per grm. of the oxide. It appears, therefore, that the oxide of cadmium does not lose its gas, either under water in a vacuum or under boiling water at atmospheric pressure.

Two experiments were made to determine whether oxide of cadmium still retains gas when heated to a temperature at which it begins to volatilise. The oxide was reduced to constant weight, and then, by substituting common blast-lamps for those ordinarily used, the temperature of the furnace was raised to a point lying between the fusing temperatures of pure silver (960°) and potassium sulphate (1066°). At this temperature the oxide lost in weight, very slowly, but nevertheless steadily; and the white porcelain of the crucibles became tarnished with a yellow coating, proving unmistakably that sublimation had begun.

Both samples of the oxide were four times re-heated, each time for six hours, and weighed after each heating. The separate losses were very minute; and, altogether, they amounted only to 1 m.grm. in one case and to 0·57 m.grm. in the other, showing that we had not exceeded the temperature of initial volatilisation. When these specimens of oxide were afterwards dissolved in a vacuum,

one of them gave 0·240 c.c. and the other 0·247 c.c. of gas per grm. of oxide.

The gas from the oxide of cadmium was examined spectroscopically, after removal of the oxygen, and found to be nitrogen.—*American Chemical Journal*, xx., No. 7, July, 1898.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 94).

Zirconium.

This element is rarely looked for by chemists, though shown by the microscope to be one of the most constant rock constituents, usually in the form of zircon, in which occurrence its amount can be approximately judged of and a chemical test rendered almost unnecessary; but sometimes it occurs in other minerals, and is then unrecognisable under the microscope. It may rarely be presented up to a few tenths of 1 per cent of the rock.

For its detection and estimation in such cases, or whenever a search for it seems called for, the following procedure has been devised, which serves when carried out with care, to detect with certainty the merest trace—0·02 per cent, for instance—in 1 grm.

The powder is thoroughly fused with sodium carbonate, leached with water, the residue dissolved in a little hot dilute sulphuric acid, and filtered through the original filter, which is ignited, evaporated with hydrofluoric and sulphuric acids, and its solution added to the main one after filtration from any barium sulphate that may appear. To the solution, which should be in a small flask and contain not much above 1 per cent of pure sulphuric acid, is now added hydrogen peroxide to oxidise the titanium, and then a few drops of a soluble orthophosphate solution. The flask is then set aside in the cold for twenty-four to forty-eight hours. If the colour bleaches after a time, more hydrogen peroxide should be added. Under these circumstances the zirconium is thrown out as phosphate and collects as a flocculent precipitate, which, at this stage is not always pure. No matter how small or insignificant, it is collected on a filter, ignited, fused with sodium carbonate, leached with water, the filter again ignited, fused with very little acid potassium sulphate, brought into solution in hot water with a few drops of dilute sulphuric acid, poured into a flask of about 20 c.c. capacity, a few drops of hydrogen peroxide and of sodium phosphate added, and the flask set aside. Titanium is now almost never present, and the zirconium appears after a time as a white flocculent precipitate, which can be collected and weighed as phosphate. For the small amounts usually met with it is safe to assume that it contains 50 per cent of ZrO_2 (51·8 by theory). If the amount is rather large, it may be fused with sodium carbonate, leached, ignited, fused with acid potassium sulphate, reprecipitated by ammonia, and weighed as ZrO_2. Certainty as to its identity can be had by again bringing it into solution, precipitating by ammonia, dissolving in hydrochloric acid, evaporating to a drop or two, and testing with turmeric paper. With the very smallest amounts no colour can be obtained by the turmeric paper test, which, however, is readily available for as little as 1 milligrm, ZrO_2, and with the proper care for as small an amount as 0·3 milligrm. (Dr. H. N. Stokes). No element other than thorium is ever likely to contaminate the ZrO_2 thus precipitated.

This separation of zirconium from titanium in presence of hydrogen peroxide is founded on a method by G. H. Bailey (*Journ. Chem. Soc.*, vol. xlix., pp. 149, 481, 1886), but in his experiments the precipitation was not made by addition of a phosphate, but is said to be due solely to the hydrogen peroxide, the precipitate being a hydrated peroxide, Zr_2O_5 or ZrO_3 (Bailey, Chemical News, vol. lx., p. 6, 1889). My own efforts to secure a precipitate in acid solutions of zirconium sulphate by hydrogen peroxide alone were unsuccessful, perhaps for lack of a sufficiently strong peroxide. The ability to obtain the zirconium free from phosphoric acid would certainly be a great improvement on the method described above.

Were it not for the necessity of working in a much too acid solution, the separation of zirconium could be made in the same portion in which the titanium is colorimetrically determined.

Davis (*Am. Chem. Journ.*, vol. xi., p. 27, 1889), separates zirconium sharply from aluminum, but not from iron, by precipitation as an oxyiodate in a boiling neutralised solution of chlorides, but the method is hardly applicable for rock analysis.

Baskerville (*Journ. Am. Chem. Soc.*, vol. xvi., p. 475, 1894; Chemical News, vol. lxx., p. 57, 1894), has proposed a method for the separation of zirconium from iron and aluminum similar to his method for the separation of titanium from those elements (see *ante*). It is based on the precipitability of ZrO_2 by boiling the neutralised chloride solution for two minutes in presence of sulphurous acid, and seems to be excellent. As titanium is always present and is presumably quantitatively thrown down also, the two would have to be separated by hydrogen peroxide. No tests as to the availability of the method for separating the small amounts met with in rock analysis have been made.

Rare Earths other than Zirconia.

For the few cases in which it may be necessary to look for rare earths other than zirconia, the following procedure is suggested as likely to prove satisfactory in many cases:—

The rock powder is thoroughly decomposed by several partial evaporations with hydrofluoric acid, the fluorides of all earth metals except zirconium are collected on a platinum cone, washed with water acidulated by hydrofluoric acid, and the precipitate washed back into the dish or crucible and evaporated with enough sulphuric acid to expel all fluorine. The filter is burned and added. By careful heating the excess of sulphuric acid is removed and the sulphates are taken up by dilute hydrochloric acid. The rare earths, with perhaps some alumina, are then separated by ammonia, washed, re-dissolved in hydrochloric acid, and evaporated to dryness, then taken up with water and a drop of hydrochloric acid, and only enough ammonium acetate to neutralise the latter acid, followed by oxalic acid. In this way as little as 0·03 per cent of rare earths have been found when working on not more than 2 grms. of materials.

This method eliminates at once most of the aluminum, the iron, phosphorus, titanium, and zirconium, and has the further advantage of collecting with the earthy fluorides as UF_4 any uranous uranium that the rock might have held.

An alternative method would be to fuse with sodium carbonate, leach with water to get rid of phosphorus as far as possible, dissolve the residue in hydrochloric acid, separate silica as usual, precipitate alumina, &c., by ammonia, dissolve the precipitate again in hydrochloric acid, evaporate, and proceed as by the former method, which in most cases would undoubtedly give better results than this one.

Chromium, Phosphorus.

Silica is removed by hydrofluoric and sulphuric acids, excess of fluorine expelled, the residue brought into solution as far as possible with hydrochloric acid and hot water, filtered, the residue ignited, fused with sodium carbonate dissolved in hydrochloric acid, and the solution added to the main one, which is now precipitated by ammonia to get rid of the magnesium salts usually present

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

and thus insure a cleaner subsequent fusion with sodium carbonate.

Separation of Alumina and Phosphoric Acid.—The precipitated Al_2O_3, P_2O_5, Cr_2O_3, Fe_2O_3, and TiO_2 is dissolved in hot hydrochloric acid and filtered into a large platinum crucible, the filter burned and added, the solution evaporated to pastiness, a little water added to dissolve the salts, and dry sodium carbonate added in portions and stirred in thoroughly to prevent lumpiness in the fusion to follow, which is continued for half an hour. Addition of sodium nitrate is not necessary. The melt is boiled out with water, and to the filtrate containing all the chromium and phosphoric acid and most of the aluminum ammonium nitrate is added till no further precipitation ensues. All P_2O_5 is thus removed, but not quite all alumina. After decanting, the precipitate is washed with ammonium nitrate solution, dissolved in nitric acid, and the phosphoric acid thrown out by molybdate solution.

Chromium.—The previous filtrate is acidified, boiled, rendered ammoniacal, and hydrogen sulphide introduced or fresh ammonium sulphide added. The precipitate of alumina and chromic oxide is now treated according to Baubigny (*Bull. Soc. Chimique*, N.S., vol. xlii., p. 291, 1884; Chemical News, vol. l., p. 18, 1885), by dissolving in hot nitric acid, evaporating to near dryness, and heating with strong nitric acid and potassium chlorate, then evaporating to dryness to get rid of the acid. On dilution with cold water, acid sodium carbonate is added in slight excess, and after two or three hours the precipitated alumina is filtered off. From the filtrate the chromium is then thrown out by fresh ammonium sulphide, redissolved to remove alkali, re-precipitated, and weighed.

Probably the separation of aluminum from chromium by hydrogen peroxide in ammoniacal solution, as recommended by Jannasch and Cloedt (*Zeitschr. fur. Anorg. Chemie*, vol. x., p. 402, 1895), would be preferable to the above if one has specially prepared hydrogen peroxide. The commercial brands are so impure that it is unsafe to employ them in most separations.

The above outline is from a paper by Dr. Chatard (*Am. Chem. Journ.*, vol. xiii., p. 106, 1891; *Bull. U.S. Geol. Survey*, No. 78, p. 87; Chemical News, vol. lxiii., p. 267, 1891), detailing a procedure devised in this laboratory for "the separation of titanium, chromium, aluminum, iron, barium, and phosphoric acid in rock analyses." If necessary, titanium, iron, and barium can be determined in the same portion, the reader being referred to the original paper for details.

Phosphorus in Rocks free from Chromium.—If the rock contains no chromium the phosphorus is determined as follows:—Fuse with sodium carbonate, dissolve in nitric acid, evaporate to dryness, take up with nitric acid, filter, ignite filter and treat with hydrofluoric and a drop of sulphuric acid, bring the small residue into solution by boiling with nitric acid and to the main portion, in which, after addition of ammonium nitrate, precipitate by ammonium molybdate solution. The turbidity often observed on dissolving the precipitated phosphomolybdate in ammonia is due to a compound of phosphorus which should always be re-fused with sodium carbonate and treated as above, in order to recover the phosphorus in it, if the addition of a small fragment of a crystal of citric or tartaric acid fails to dissolve it.

It is sometimes possible to extract all phosphorus from a rock by simple digestion with nitric acid; but quite as often, if not more often, this fails, and hence the necessity for resorting to the longer method.

Ferrous Iron.

Comparison of Sealed-tube and Hydrofluoric-acid Methods.—No point in rock analysis has been the cause of greater solicitude to the chemist, and especially to the mineralogist and petrographer, than the determination of iron in ferrous condition. The sealed-tube method with sulphuric acid, for a long time the only available one, is in theory perfect, since complete exclusion of oxygen is easily attainable. Its chief defect, however, lies in the inability to always secure complete decomposition of the iron-bearing minerals, and even to ascertain, oftentimes, whether or not the decomposition has been complete. The addition of hydrofluoric acid to the sulphuric in the tube, in order to insure this breaking up, is to be regarded as of very doubtful utility in most cases, since the glass may be so strongly attacked as to add an appreciable amount of iron to the solution, and the hydrofluoric acid may have exhausted itself in attacking the glass before the more refractory minerals succumb. Nevertheless, if decomposition can be effected by sulphuric acid alone the results obtained are sharp and concordant, and what is especially remarkable, and up to the present without a satisfactory explanation, they are in rock analyses invariably higher than when made by any of the modifications of the hydrofluoric-acid method now so extensively practised. This difference is not very marked with rocks containing but 1 or 2 per cent of the ferrous iron, but it increases with rising percentage to such an extent that where the sealed-tube method will show 12 per cent FeO the other may indicate no more than 10 per cent. This is a fact of which the writer has long been cognisant, but it does not seem to be known to chemists or petrographers at large, and it is one well deserving of critical examination. Attempts have from time to time been made to get at a solution of the problem, but without effect. Experiments with soluble iron salts of known composition, like ferrous sulphate or ferrous ammonium sulphate, throw no light on the subject, for both methods give the same sharp and accurate results with them. It is only when a silicate is taken that the difference appears. In titrating for ferrous iron the well-known rapid bleaching of the first permanent colour—the supposed crucial test of complete oxidation—in hydrofluoric-acid solutions of silicates, even with sulphuric acid present, has been thought to be perhaps in some way connected therewith. This bleaching is so pronounced that several c.c. of permanganate solution may be gradually added after the first so-called permanent colouration, without its being possible to obtain a persistent colour; and yet in hydrofluoric-sulphuric solutions of ferrous salts free from silica the first colouration is persistent for a long time.

The question now arises, which of these methods gives the correct result? My own opinion is in favour of the sealed-tube method with sulphuric acid, simply for the reason that there seems no possible chance for obtaining too high results thereby. No suggestion ever advanced to account for their being too high seems tenable. It has been proved over and over again that the error is not due to iron from the glass or to impurities in the sulphuric acid; a reduction of sulphuric acid with corresponding oxidation of ferrous iron seems impossible; and yet, did it occur, the result could be in nowise affected, for the amount of permanganate needed would be the same.

Notwithstanding this predilection in favour of the tube method, the one in exclusive use in this laboratory is that by decomposition by means of hydrofluoric and sulphuric acids. The results obtained by it are at least comparable with those found by other workers, and the impossibility of being assured of complete decomposition in a sealed tube is sufficient to condemn that method for general use.

Cooke's Method of Decomposing by Hydrofluoric and Sulphuric Acids.—The specially ground powder, in a capacious crucible, is placed, after stirring up with dilute sulphuric acid, on a small water-bath of a single opening, and covered with a glass funnel which rests in a depression of the cover, into which water constantly drops from a tubulated bottle, thus securing a perfect water-joint and serving to keep the bath full. Through a small metal pipe carbonic acid gas flows into the bath above the surface of the water, and rising through orifices in the cover fills the funnel and crucible (J. P. Cooke, *Am. Jour. Sci.*, 2nd ser., xliv., p. 347, 1867). The lamp under the bath is lighted, and hydrofluoric acid is poured into the crucible through a platinum funnel, which is left in place

to serve as an occasional stirrer, for which a rod or wire may be substituted. After boiling commences the rapid gas current can be safely interrupted, to be restored when the lamp is extinguished after one-half to one or more hours. A full stream of cold water is then caused to flow from the tubulated bottle into the bath, the overflow from the outlet tube being caught in a receiver. As soon as cool the contents of the crucible are emptied into a platinum dish containing cold water, and titrated till the first permanent colour appears, which usually will last for only a few seconds. Duplicate determinations are to be advised whenever possible, since even with the utmost care the results will occasionally differ more than is allowable.

Pratt's Modification of the Hydrofluoric-acid Method.—J. H. Pratt (*Am. Jour. Sci.*, 3rd ser., xlviii., p. 149, 1894) has shown that very satisfactory ferrous iron determinations can be secured by simple boiling of the rock powder with hydrofluoric and sulphuric acids in a large crucible fitted with a cover and platinum tube for introduction of carbon dioxide. His test experiments on ferrous sulphate show that there need be practically no oxidation, even if the heating lasts several hours. The directions given in his paper (p. 150), with reference to the treatment of very refractory minerals which are not fully decomposed by this treatment, must be understood as referring only to homogeneous minerals and not to rocks, where the relations of ferrous and ferric iron in the undecomposed portion are certainly different from those in the part dissolved.

Influence of Sulphides.—The presence of pyrite or marcasite is probably without serious effect on the ferrous-iron determination by any of the hydrofluoric-acid methods. These sulphides are very resistant toward attack in the absence of oxygen, as is shown by the fact that if present in any quantity they can be readily recognised in the residue after titration. In any case it is impossible to allow for an error introduced by their possible decomposition, and the result of titration must count as ferrous iron. In the case of soluble sulphides two sources of error are introduced—that of reduction of ferric iron by hydrogen sulphide evolved, and that due to the ferrous iron which the sulphides themselves may contain especially if pyrrhotite is present. The first of these is perhaps negligible, since most of the hydrogen sulphide would probably be expelled without reducing iron. The second is approximately measurable if it is known that pyrrhotite is the only soluble sulphide present and its amount has been ascertained by determining the hydrogen sulphide set free on boiling with hydrochloric acid in a current of carbon dioxide. In this case a correction is to be applied to the result of titration for total ferrous iron. (See also under Sulphur).

(To be continued).

CORRESPONDENCE.

THE KINETIC IMAGINING OF GASES.

To the Editor of the Chemical News.

SIR,—Mr. Emmens appears to be not well pleased with the review of the pamphlet "The Kinetic Imagining of Gases" which recently appeared in your journal, and seems desirous of discussing the matter further with me.

If this is his desire, I must decline to gratify him, for it does not appear to me that any good can result from arguing with a man who is not only ignorant of the fact (among others) that the earth rotates on its axis every year once more than the number of days in the year, but is so lacking in intelligence as to be unable to appreciate the fact when it is pointed out to him.—I am, &c.,

THE WRITER OF THE REVIEW.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
No. 4, 1898.

Action of Oxalic Diethyl Ethers on *p*-Amidophenol and its Ether.—A. Piulti and R. Piccoli.—When oxalic ether and *p*-amidophenol are heated at 160° for an hour in sealed tubes, a substance is formed, soluble in hot water and acetic acid, with melting-point 184—185°, which analysis proves to be *p*-oxyphenyloxamine,—

$$C_2H_5.OOC.CO.NH.C_6H_4.OH.$$

p-Methoxyphenyloxaminic ester, crystallising in long white needles and melting at 108—109°, is prepared by acting on *p*-anisidine with oxalic ester and extracting with hot water. *p*-Ethyloxyphenylaminic ester is formed when oxalic ester acts on *p*-phenetidine; it crystallises in bright hexagonal plates (m. p. 108—110°), which are soluble in hot water, alcohol, and acetic acid.

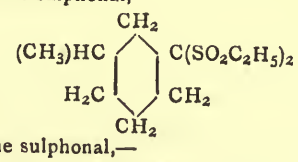
Sulphonated Cyclic Ketones.—O. Wallach and Walther Borsche.—The authors have prepared pentanone sulphonal,—

$$\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\!\!>\!C.(SO_2C_2H_5)_2;$$

methylpentanone sulphonal,—

$$\begin{matrix}CH(CH_3).CH_2\\CH_2\text{——}CH_2\end{matrix}\!\!>\!C(SO_2C_2H_5)_2;$$

methylhexanone sulphonal,—



and heptanone sulphonal,—

$$\begin{matrix}CH_2.CH_2.CH_2\\CH_2.CH_2CH_2\end{matrix}\!\!>\!C(SO_2C_2H_5)_2$$

by the action of mercaptan on the penta-, hexa-, and hepta-cyclic ketones.

Diazonium Hydrate in Aqueous Solution.—A. Hantzsch.—The author finds that the best method of preparing pure diazonium hydrate solution was by dissolving pure diazonium chloride in water, and shaking this up with the calculated quantity of silver oxide whilst keeping it cooled in ice. The solution is very unstable, being a clear bright yellow solution at 0°, but becoming reddish brown at ordinary temperatures with separation of a flocculent resin. With silver nitrate a brown precipitate is formed; with mercuric chloride, a precipitate soluble in excess.

Formation of Metallic Sodium from Sodium Peroxide.—Heinrich Bamberger.—The author prepares metallic sodium in the following ways:—(1). Na_2O_2 and charcoal are well powdered and heated in a crucible to 300—400°. The following reaction takes place:—$3Na_2O_2+2C=2Na_2CO_3+Na_2$. The reaction is violent, the sodium being found condensed on cooling on the lid and upper part of the crucible. (2). Na_2O_2 and CaC_2 are heated together, the reaction taking place with explosive violence according to the equation $7Na_2O_2+2CaC_2=2CaO+4Na_2CO_3+3Na_2$.

Action of Acetic Anhydride on the Anilides of Dibasic Acids.—H. v. Pechmann and Wilh. Schmitz.

Nitrogen Derivatives of Benzylacetophenones.—T. Tambor and F. Wildi.

Paradinitrodibenzyldisulphonic Acid.—C. Rio and C. Simon.

Some Esters and a Crystalline Pseudo-ester of Rhodinol.—Ernst Erdmann.

Investigations on Optic Activity.—L. Tchúgaeff.

The 3-Oxy-1 . 2. 4-triazoles, and some Acidylsemicarbazides.—O. Widman and Astrid Cleve.

Action of Anilines on Dioxytartaric Acid.—Arnold Reissert.

Action of Oxalic Ester and Sodium Ethylate on Substituted Nitrotoluoles. — Arnold Reissert and J. Scherk.

Action of Oxalic Ester and Sodium Ethylate on Nitrocresolmethyl Ether ($OCH_3 : CH_3 : NO_2$ = 1 : 3 : 6).—Arnold Reissert.

Derivatives of Cycloheptanes.—Eduard Buchner and Andreas Jacobi.

β-Isophenylacetic Acid. — Eduard Buchner and Ferdinand Lingg.

Choline and Trigonelline in the Seeds of Strophanthus kombé.—Hermann Thoms.

Alkyl-sulphonic Acid Salts.—Arthur Rosenheim and Otto Liebknecht.

Action of *o*-Xylylenbromide on Primary, Secondary, and Tertiary Amines.—M. Scholtz.

Synthesis of Xanthines from Hydrocyanic Acid.—Armand Gautier.

New Method of Molecular Weight Determination by the Boiling-point Method.—W. Landsberger.

Method of Formation of *p*-1-Nitrodiphenyltetrazols.—Edgar Wedekind.

Journal de Pharmacie et de Chimie,
Series 6, vol. vii., No. 10.

The Gelatinous Matter (Pectine) in Gentian Root.—MM. E. Bourquelot and H. Herissey.—Most pharmacopœias recommend maceration for the preparation of the aqueous extract of gentian, but there is a gelatinous body present which has no therapeutic properties, and which renders filtration difficult. It has been isolated by digesting for three quarters of an hour at from 80°—90° in water acidulated with hydrochloric acid; the clear liquid is then precipitated by alcohol at 90°. The jelly thus obtained is strained through fine muslin, washed with alcohol, then re-dissolved in water and again precipitated by alcohol; after a final washing with ether the product was dried between sheets of filter paper, and then in the air. The results of some experiments showed that there must be either some resinous body present in the gentian root which has the power of preventing its solution in water, or that pectose, susceptible during desiccation or trituration of being transformed from soluble pectine into insoluble pectic acid, is present. The authors eventually found that with a mineral acid, a very different product was obtained to that got by water only. It is possible in the first case to obtain a pectine mixed with hydrates of carbon strongly dextrogyre, separated by the acid from the cellular membrane.

Formulæ for the Rapid Estimation by Duclaux's Method of the Volatile Acid Products of a Fermentation.—MM. Bordas and De Raczkowski.—A purely mathematical paper not suitable for abstraction.

CARPENTERS' COMPANY'S TECHNICAL INSTITUTE,
STRATFORD, E.

EVENING CLASSES are held in Inorganic and Organic Chemistry, Theory and Practical. Prospectus containing details on application.

The Principal (W. Ping) conducts a Special Class in Advanced Work (Honours, S.K.).

The Sulphate of Ammonia Committee
OFFER
THE SUM OF 500 GUINEAS

To be given for the best Essay on the following subject:—

"THE UTILITY OF SULPHATE OF AMMONIA IN AGRICULTURE."

The subject to be treated from a practical and scientific point of view.

The Committee has secured the services of Mr. William C. Little, Member of the late Royal Commissions on Agriculture, and Dr. Voelcker, Consulting Chemist to the Royal Agricultural Society of England, to act as Judges of the Essays sent in. In the event of any difference arising, Mr. Samuel Rowlandson, a Member of the Council of the Royal Agricultural Society of England, will act as referee.

The Essays must be in the English language, and written on one side of the paper only; they must further bear a distinguishing motto or nom de plume, but not the names of the authors.

Each author, when sending in his Essay, must at the same time write his name and address on a slip, which he shall enclose in a separate envelope, seal the letter, and write outside it the motto or nom de plume he adopts for his Essay. The Essay and the envelope containing the slip to be sent in, under one cover, to the undersigned.

The envelopes containing the names of the authors will be opened in the presence of the Committee after the Judges have made their award.

All Essays must be in the hands of the undersigned not later than November 15th, 1898. The selected Essay will become the property of the Committee, who reserve to themselves the right to make such use of it as they may think fit.

The Committee also reserves to itself the right to purchase for a sum not exceeding fifty guineas any of the other Essays.

W. G. BLAGDEN (*Chairman*),
4, Fenchurch Avenue, London, E.C.

HERIOT-WATT COLLEGE, EDINBURGH.

F. GRANT OGILVIE, M.A., B.Sc., F.R.S.E., Principal.

DAY CLASSES—SESSION 1898-99.

The SESSION extends from TUESDAY, October 4th, 1898, to Friday, June 2nd, 1899.

These classes provide Courses of Study extending over one or more years, suitable for Students who have previously passed through the Curriculum of a Secondary School. The principal Courses are:—Physical and Chemical, Mechanical Engineering and Electrical Engineering. There are also classes in French, German, Drawing, and Practice of Commerce. Class Fees from £1 1s. to £4 4s.; Session Fee, £10 10s.

There is also a preparatory Course of Instruction for Agricultural Students; Session Fee, £5 5s. An extract from the Calendar of the College giving particulars of the Day Classes, and of the various Appliances, Laboratories, and Workshops available for instruction, may be had on application to the Librarian, at the College, or to the Treasurer of George Heriot's Trust.

DAVID LEWIS,
Treasurer.

Treasurer's Chambers, 20, York Place, Edinburgh, July 18th, 1898.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2023.

(STUDENTS' NUMBER).

ADDRESS TO STUDENTS.

It is once more our duty to indite a few remarks, intended more especially for those among our readers who are about to take one of the most important steps which will influence their future career. We chiefly address those Students who, having made choice of a profession, are, within the next few weeks, about to enter on the actual work of learning it. At school they have had, we hope, the necessary training to get "fit"—they have now to realise the necessity for work, and be it remembered that, in these days of advanced and rapidly expanding science, he who loses time at the beginning runs a great risk of being left behind in the race.

Specialism is the order of the day, and the sooner the Student finds out which particular branch of science is best suited to his taste and opportunities, the sooner will he be able to stand in line with the masters of that subject.

It must not be imagined that we are advising narrowness of study; on the contrary, the widest read man has the greatest aptitude for absorbing and digesting new ideas.

We cannot too strongly urge on every Student to make use of all his opportunities for acquiring knowledge, and, above all, never to forget that the final examination is *not* the be-all and end-all of the course of instruction he is about to enter upon.

As the cautious Alpine climber makes sure that one foot is firmly placed before he takes another step forward, still keeping the summit in view, so must the seeker after success make sure that his groundwork is solid; at school he learns how to learn, at College he learns, but in after life he has to find out and teach himself: this will be made easier if he remembers that, no matter how many competitors there are, there is always room on the top.

We cannot close these remarks without expressing our regret that the authorities at the War Office have decided to do away with part of the scientific training at the Royal Military College at Woolwich, by closing the chemical laboratory: this is decidedly a movement to the rear.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages: — Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Sound, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in

the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a two days' practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examiantion, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Christ Church Laboratory.—A. Vernon Harcourt, F.R.S.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

Trinity College.

Professor of Chemistry—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—J. Percy Bailey, B.A.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures ofthe Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered :—

1. *Inorganic Chemistry and Chemical Philosophy.* — Elementary, first year; advanced, second year.
2. *Organic Chemistry.* — General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(Division of Engineering, Architecture, and Applied Science).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.
Demonstrator of Practical Chemistry—Herbert Jackson, F.C.S.
Assistant Demonstrator—P. H. Kirkaldy, F.C.S.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1898-99 are October 4, January 18, and April 26.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *viva voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. 0d.; per ann., £8 8s. 0d.; Practical Chemistry per term, £4 4s. 0d.; per ann., £10 10s. 0d.; Experimental and Analytical Chemistry —Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

Metallurgy.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Photography.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

Evening Classes.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

Faculty of Science.

Professor—William Ramsay, LL.D., F.R.S.
Assistants—Morris Travers, D.Sc., Alexander Kellas, B.Sc., and E. C. C. Baly, F.I.C.

The Session is divided into three Terms, as follows, all the dates being inclusive :—

First Term, from Tuesday, October 4th, until Friday, December 16th;

Second Term, from Tuesday, January 10th, 1899, till Friday, March 24th;

Third Term, from Tuesday, April 18th, till Friday, June 30th. Class Examinations begin on June 19th.

Junior Courses of Inorganic Chemistry.

First Term: Tuesday, Thursday, and Saturday at 10. Latter half of Second and Third Term: Tuesday, Thursday, and Saturday. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 10. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday, Thursday, and Saturday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Tuesday and Thursday at 9, and Saturday at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course besides the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for the Second and Third Terms, £4 14s. 6d.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1898-99; also the Clothworker's Scholarship of £30.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—W. P. Wynne, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and M. O. Forster, Ph.D.

Assistants—G. S. Newth and G. T. Morgan, B.Sc.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 6th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics	2	3

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Model and Free-hand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half fees.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Bona fide teachers qualified to earn payments for teaching Science according to the rule of the Science and Art Directory may obtain permission to attend free any course of lectures.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses. (See Science and Art Directory).

Working Men's Lectures.—Notification of these will be given in the newspapers,

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-seventh Session will commence on Monday, October 3rd, 1898.

Professors—Chemistry, J. Norman Collie, Ph.D., F.R.S. (Dean); Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Materia Medica and Pharmacy, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

Assistant Lecturer and Demonstrator—A. W. Warrington, M.Sc. (Vic.)., F.I.C.

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, October 4, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Pass Course; four lectures weekly during the Lent and Easter Terms. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, two lectures weekly on Chemical Theory. (Courses A and B will generally be given in alternate Sessions; for 1898-9, Course B.) (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 20, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Fred. Marsden, Ph.D., M.Sc. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton.

Physics. — Professor, Andrew Gray, M.A., LL.D., F.R.S.

The Session opens October 4th, 1898. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Advanced Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Fee, £4 4s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 3rd, and terminates on June 23rd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures

held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 90 lectures on Chemical Theory; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.
Lecturer—Francis E. Francis, B.Sc., Ph.D.
Demonstrator—D. H. Jackson, M.A., B.Sc., Ph.D.

The session 1898-99 will begin on October 4th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

Day Lectures.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Junior Course.—Two Lectures a week will be given during the First and Second Terms. Fee, £3 3s.

General Elementary Science (London Matriculation).—A course of about 16 Lectures will be delivered in the Third Term. Fee, including Physics (1st and 2nd Terms), £5 5.

Special Course.—A special course of Lectures is also given to Engineering Students.

Senior Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Junior and Senior Courses.

Advanced Course (Parts I. and II.).—One Lecture a week will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given during the Second Term, and three Lectures a week during the Third Term. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	15	12½	10	7½	5
,, Two Terms ..	11	9	7½	5½	3½
,, One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

Evening Lectures.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

General Elementary Science.—A course of Lectures, primarily intended for Candidates for Matriculation, will be given during the First Term. Fee (including Physics), 7s. 6d.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open on Tuesday and Wednesday evenings from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

MASON COLLEGE, BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., B.Sc., F.R.S.
Assistant Lecturer—C. F. Baker, Ph.D., B.Sc.
Demonstrator—W. R. Innes, Ph.D., M.Sc.
Lecturer on Metallurgy—Godfrey Melland, F.I.C.

The Session will be opened on October 4th, 1898.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. Lecture days—Wednesdays and Fridays at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend this Course before entering for the General Course. Candidates for the Matriculation Examination of the University of London also are advised to attend this Course.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Wednesday, and Friday at 12 noon Fee, £1 11s. 6d.

The General Course (including Inorganic and Organic lectures) qualifies for graduation in the medical faculties of the universities of Edinburgh, Glasgow, Aberdeen, and Durham.

Special Courses of Lectures and of Laboratory Instruction are given for Medical Students preparing for the Conjoint Board Examinations.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees :—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 „	8½ „
Three Terms	18 „	12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Special Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of £100 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of £100 is awarded annually in September.

Forster Research Scholarship.—A Scholarship of the value of £50 is annually awarded.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD TECHNICAL COLLEGE.

Chemistry and Dyeing Department.

Head Master—W. M. Gardner, F.C.S.
Demonstrator and Lecturer on Geology—A. B. Knaggs, F.C.S.
Lecturer on Botany and Biology—William West, F.L.S.

The College Session is divided into three terms. The Session commences on September 12th and terminates on July 15th. The course of instruction extends over three years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Fee, £5 per Term, or £13 per Session.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day.

A General Course preparing for the Pharmaceutical Society's examinations has been arranged.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.
Assistants—Cecil C. Duncan, F.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College

Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.
THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc. Lond., F.I.C.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D., F.I.C.

Assistant Lecturer and Demonstrator—Herbert Ingle, F.I.C.

Demonstrators—T. S. Patterson, Ph.D., and J. McCrae, Ph.D.

The Session begins October 11, 1898.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry. — Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Organic Chemistry Honours Course. — Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.

6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.— Tuesday during the First Term, at 4 p.m.

8. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.

9. Agricultural Chemistry.—Mondays, Wednesdays, and Fridays at 2 p.m.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Evening Class.

A short Course of Lectures by Prof. Smithells, on the Chemistry of Artificial Lighting will be given during the first Term. Fee, 10s. 6d.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.

Lecturer and Research Assistant — A. G. Perkin, F.R.S.E.

Assistant Lecturer—R. B. Brown.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Demonstrator—M. C. Lamb.

The full Course, which extends over a period of two years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—J. R. Campbell, B.Sc.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry — C. A. Kohn, B.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers — T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., and A. W. Titherley, M.Sc., Ph.D.

Assistant—H. H. Froysell.

The Session commences October 4th.

Entrance Scholarship Examination takes place early in May each year.

The William Gossage Chemical Laboratory has been completed and opened for Advanced Students, the Metallurgical Laboratory has been enlarged, and new Gas Analysis and Electro-Chemical rooms have been added, with a third Lecture Room.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3 10s.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F. — Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metullurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electrochemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Saitanry subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work.

The William Gossage Laboratory, opened in 1897, consists of a large and well-fitted general Laboratory for advanced Students, a new gas analysis room, an additional lecture-room for Metallurgy and other classes, and an addition to the Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Four days	9	16 10s.
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course E or D, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—Courses D, F, and H. Any other Courses omitted in a previous year. Laboratory, five days per week. Gas Analysis, Water Analysis, Electrochemistry. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B. Sc. Degree in the Honours School of Chemistry.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1898, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held on Chemistry, Metallurgy, and on Electro-chemistry.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—Saville Shaw, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturer and Demonstrator—F. C. Garrett, M.Sc., F.C.S.

Demonstrator—J. Cooper, B.Sc.

The Session will commence on September 26th, 1898.

Lectures begin on October 4th, 1898.

1. *General Course.* — This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 5th. Fee, £3 10s. for the Session.

Second Year Course.—The Lectures for the second year students cousist of a course of Lectures on Inorganic Chemistry, extending from October to December, and a course of Lectures on Organic Chemistry from January to the end of the Session. The Class will meet on Tuesdays and Thursdays at 11 a.m., and Fridays at 3 p.m., and will commence on October 6th. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m.

Metallurgy and Assaying.—Lecturer, Saville Shaw, M.Sc., F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects

professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Wednesday, September 29th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students, including Johnston Chemical Scholarship of the value of £60 for one year.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; P. J. Hartog, B.Sc.; E. J. Russell, B.Sc.; and D. S. Jerdan, B.Sc.

Demonstrator in Organic Chemistry—W. T. Lawrence, B.A., Ph.D.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Assistant Lecturer in Metallurgy—J. Crowther.

The Session begins on October 4, 1898, and ends on July 1, 1899.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

METALLURGY.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: The Laboratory will be open to students every day.

The Chemical Laboratories are open daily from 9.30. a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the *College* Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the John Buckley Scholarship; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—J. J. Sudborough, D.Sc., Ph.D., F.I.C., and R. M. Caven, B.Sc., F.I.C.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 10th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., six hours 30s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor Examinations. Special lectures will also be given in Chemistry and Materia Medica.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in September. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

An Agricultural Course of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Demonstrators and Lecturers — G. Young, Ph.D., and L. T. O'Shea, B.Sc., F.C.S.,

The Session will commence on October 6th.

Beginners' Course.—Inorganic Chemistry: Tuesday from 10 to 11 a.m. Fee, £1 11s. 6d.

Matriculation Course.—Friday 10 to 11. Fee, £1 11s. 6d.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 11s. 6d. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s. Chemistry of the Colouring Matters: Fridays, 12 to 1; fee, £1 11s. 6d.

Physical Chemistry.—Monday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy. — Thursday, 11 to 12. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on the Chemistry of Coal Mining.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc.

Assistant Lecturers—J. S. Lumsden, Ph.D., B.Sc., and J. K. Wood, B.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 12th, and ends on March 22nd. The Summer Session extends from the middle of April to the end of June.

The First Year's Lecture Course on Systematic Chemistry is given daily during the Winter Session, and

embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh. The Courses are suitable for the degrees of the University of London and for the Civil Service appointments, and will also satisfy the requirements of Students in Pharmacy, and of Students who intend to become candidates for the Associateship of the Institute of Chemistry, as far as qualification in Chemistry is concerned.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D., and H. Marshall, D.Sc.

Assistants—W. W. Taylor, M.A., B.Sc., and J. P. Longstaff.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to end of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. A class on Organic Chemistry is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are given by the Assistants on some particular branch of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-Dec., Jan.-March; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. Practical Examination:—Complex Qualitative Analysis; Inorganic and Organic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on any two of the following subjects, selected by himself:—Ultimate Organic Analysis; Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—F. Grant Ogilvie, M.A., B.Sc.

Professor—John Gibson, Ph.D., F.R.S.E.

Demonstrators—Andrew F. King and James B. Shand.

The Session begins October 4th, 1898.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

Chemistry.—The first course for day students is a combination of Lectures with Laboratory instruction. In the Lectures some of the more important elements and their compounds are discussed in detail, so as to lead to a knowledge of the general laws of chemical action. Other important elements are treated in less detail, and the relations and classification of the elements generally are broadly indicated. In the Laboratory each student will receive instruction in general chemical manipulation, in accurate weighing, volumetric measurements, and in some of the simpler methods of quantitative analysis. After making a series of simple preparations, he works through a number of experimental exercises illustrating chemical combination, oxidation, reduction, and double decomposition. These exercises are followed by instruction in simple methods of qualitative analysis, especial attention being given to dry way testing and the use of the spectroscope. Students attending a further course may take up the study of systematic analysis, and extend the knowledge they have gained of quantitative analysis by exercises in gravimetric, volumetric, and electrolytic methods. Ultimately they may make a speciality of any branch of the subject which may be most necessary for their future work. Great attention has been paid to the thorough equipment of Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the

Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—E. J. Mills, D.Sc., F.R.S.
Agricultural Chemistry Lecturer—John W. Paterson, B.Sc., Ph.D.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction in Metallurgy and Mining will be given in both Day and Evening Classes.

Copies of the Calendar for 1896-97 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

United College of St. Leonard and St. Salvator.

Professor of Chemistry — T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 12th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about fifty Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 30th and following days. About thirty of these Bursaries are restricted to Men and about twenty to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. Two, of £40 each, are open to students of either sex. Two Scholarships of £100 each, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1897-98. A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry, and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

The Session commences on Tuesday, October 19, 1897.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

Scholarships.—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.
Demonstrator—R. E. Doran, F.C.S.

The College Session begins on October 18th, 1898, and ends on June 10th, 1899. The classes are open to male and female students.

Systematic Chemistry.—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical

Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.—(1) Two ordinary Courses of Practical Chemistry will be held, each of three months' duration; one commencing on January 5th, 1899, and adapted to the requirements of Students proceeding to the Examinations of the Royal University of Ireland; the other ending about the third week in June, and suitable for Medical Students intending to present themselves for the Examinations of other Licensing Bodies. Fee for each Sessional Course, £3. (2) A Course for Pharmaceutical Students will be held in the second and third terms; fee, £5. (3) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., F.I.C.

Demonstrator—W. S. Mills.

The College Session, 1898-99, commences October 18th and ends June 10th.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

For Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN. (SCIENCE AND ART DEPARTMENT).

Professor of Chemistry—W. N. Hartley, F.R.S.

Assistant Chemist—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.

Demonstrator of Chemistry and Assaying—J. Holms Pollok, B.Sc.

The Session commences on Tuesday, October 6th, 1898.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associates:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

The following are supplementary courses of instruction arranged for those who are attending a Course of Lectures:—

(1) Laboratory Instruction in the Theory of Chemistry. (2) An Analytical Course for Students in Engineering. (3) A Course of Practical Chemistry for Medical Students. (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health. (5) Assaying. (6) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net.—*City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become

Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Tuesday, Sept. 20th, and the Winter Session opens on Monday, October 3rd. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 20th, 1898. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting from the Life, and House Decoration.

City of London College, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, A.R.C.S., F.C.S. Session commences September 28.

Battersea Polytechnic.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, M.Sc., and Mr. B. C. Polkinghorne, B.Sc. Day and Evening Classes in Science and Art subjects.

Birkbeck Literary and Scientific Institution, Bream's Buildings, Chancery Lane.—Chemistry Courses will be conducted, commencing September 26, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University, by Mr. J. E. Mackenzie, Ph.D., B.Sc.

Borough Polytechnic Institute, St. George's Circus.—Lecturer, Mr. F. Mollwo Perkin, Ph.D. Lectures and Laboratory work in Chemistry and Physics. Session commences Monday, September 26, 1898.

Brixton School of Chemistry and Pharmacy, 12, Knowle Road, Brixton.—Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c. The Lectures and Classes are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to Degrees at the University of London. Medals and certificates are awarded to successful students, The Laboratory is fitted with every convenience for the prosecution of chemical studies and research. Prospectuses and further information may be obtained from the Principal.

South-West London Polytechnic, Manresa Road, Chelsea.—Principal, Herbert Tomlinson, B.A., F.R.S. Technical Day Classes in Chemical Industries, commencing September 26th.

The Goldsmiths' Institute, New Cross, S.E.—Head of the Chemistry Department, Mr. W. J. Pope; Assistants, Mr. S. J. Peachy and others. Lectures and Practical Classes in General Chemistry, also in Chemistry applied to Gas Manufacture and other industries, are held in the evenings from 7.30 to 10.0, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties.

Polytechnic Institute, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on Monday, September 26th.

Northern Polytechnic Institute, Holloway, N.—Principal, J. T. Dunn, D.Sc. Session begins September 30th. Evening Classes in Theoretical and Practical Chemistry. Assistants, Mr. H. Charles L. Bloxam and Mr. W. H. Watson, A.R.C.S.

Carpenters' Company Technical Institute, Jupp Road, Stratford, E.—Principal, William Ping. F.C.S. Session begins Monday September 26th. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School.

East London Technical College, People's Palace, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Demonstrator, F. G. Pope; Assistants, H. A. Phillips and A. J. Turner. Lectures and Practical Classes are held in the daytime in connection with the three years' course of the Day Technical College. Evening Classes are also held, offering instruction in the courses of the Science and Art Department and for the examinations of the University of London.

University Tutorial College, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Corr. Coll.).—Chemical, Biological, and Physical laboratories, open both during term and vacation. Morning, Afternoon, and Evening Classes. Students may work either for long or short periods, either for examination or for private practice. The Laboratories accommodate over 100 Students.

South London School of Pharmacy, Lim., 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., and Mr. J. Thomas, B.Sc. (Lond.), Daily, at 12 noon. Lectures on Botany daily at 1 p.m. and at 2.30 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 5, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months 12 guineas; afterwards 3 guineas per month, inclusive of all departments.

Imperial College of Chemistry and Pharmacy, 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc.

Metropolitan College of Pharmacy, 162, Kennington Park Road, S.E.—Principal, W. Watson Will, F.C.S.

Westminster College of Chemistry and Pharmacy. Trinity Square, Borough, S.E.—Messrs. Wills and Wootton. Day and Evening Classes.

The Clifton Laboratory, Berkeley Square, Bristol.—Principal, E. H. Cook, D.Sc. (Lond.), F.I.C. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations. Students are urged to undertake researches and receive special attention from the teachers. Every effort is made to produce thorough chemists rather than successful examinees.

Leeds Technical School (of the Institute of Science, Art, and Literature), Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc.(Lond.), A.R.C.S. Evening Classes are held in 30 subjects of Science and Technology, among which are:—Chemistry, Inorganic and Organic, Theoretical and Practical, by Mr. R. E. Barnett, B.Sc., A.R.C.S., and Mr. R. W. Ferguson, A.R.C.S.; Metallurgy, Theoretical and Practical, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, Heat, and Practical Physics, by Mr. J. E. Tindall, B.Sc. Fees:—Lectures, from 2s. 6d. per Session; Laboratory work, from 7s. 6d. Session commences September 12. Prospectuses

of various Classes and the complete Syllabus of the School free on application to the Secretary, Leeds Institute.

The Municipal Technical School, Princess Street, Manchester.—At this important Municipal School, with an attendance of upwards of 3500 Students, there are organised Day Courses in Pure Chemistry, with applications to Dyeing, Bleaching, Printing, Brewing, and Metallurgy. In addition there are Evening Courses, not only in Pure Chemistry, but in Metallurgy, Mineralogy, Iron and Steel Manufacture, Brewing, Bleaching, Dyeing, and Printing, Coal Tar Products, Paper Manufacture, Gas Analysis, Gas Manufacture, Chemical Engineering, Chemistry for Engineers and Builders, and Photography. The complete Syllabus (4d., by post 6d.) may be obtained on application to Mr. J. H. Reynolds, Director and Secretary, Princess Street, Manchester.

The Manchester College of Pharmacy, Oxford Street, Manchester.—Director, Mr. Charles Turner, F.C.S. Classes and Lectures specially designed to meet the requirements of Pharmaceutical Students.

Chemical and Bacteriological Laboratory, Barton Arcade, Manchester.—Mr. George J. Allen, F.C.S.—Special Instruction and Practice in Applied Science.

Higher Grade School, Patricroft.—Science and Art Day and Evening School, and Institute for Women. Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

The School of Mines, Redruth, Cornwall.—Principal and Instructor in Inorganic Chemistry, Assaying, and Mineralogy, Mr. I. Paul de Castro, B.H. (Cantab). Instructor in Mining, Thomas Collins. Instructor in Panning and Vanning, Captain W. Hambly. Instructor in Mine Surveying, Captain F. Wickett.

Sheffield Pharmaceutical and Chemical Society.—Botany and Chemistry (Theoretical and Practical), are conducted by the Professors of, and at, Firth's College, West Street, Sheffield, commencing first week in October. The Materia Medica and Pharmacy at the Society's Rooms, 37, New Surrey Street, commencing first week in October.

Hartley College, Southampton.—Principal, R. Wallace Stewart, D.Sc. (Lond.). London University Courses in Arts and Science, Science Courses for Medical and Dental Students, Mechanical and Electrical Engineering Courses. Session commences Tuesday, September 27, 1898.

Stockport Technical School.—Department of Chemistry and Dyeing.—Principal: Mr. R. J. Brown, M.Sc. A syllabus with full particulars of the courses of instruction, hours, fees, &c., is obtainable on application. Special instruction is given in the Dyeing of Felt, &c., as applied to Hat Manufacture.

Technical Institute, Salford.—Principal, W. Wilson, M.A. Session begins September 13th. Special attention is directed to the Dyeing and Calico Printing Laboratories. Day and Evening Classes.

Aberdeen University.—Prof. Japp.

School of Medicine, Edinburgh.—Dr. S. Macadam, Mr. King, Mr. I. Macadam, and Drs. Aitken and Readman.

St. Mungo's College and School of Medicine, Edinburgh.—Dr. Marshall.

Surgeon's Hall, Nicolson Street, Edinburgh.—Dr. Stevenson Macadam, Lecturer. Classes for Medical and General Students. Lectures commence Tuesday, October 12, 1897.

Glasgow University.—Prof. J. Ferguson.

Anderson's College, Glasgow.—Mr. J. R. Watson.

Veterinary College, Buccleuch Street, Glasgow.—Prof. T. S. Goodwin.—Session, October to May. Systematic Lectures on Inorganic and Organic Chemistry, daily, 12 to 1; Laboratory, daily, 10 to 5. Special Laboratory Courses arranged for Agricultural Students, October to April.

Royal College of Surgeons in Ireland, Dublin.—Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

OBITUARY.

Dr. JOHN HOPKINSON, F.R.S.

The terrible accident by which Dr. Hopkinson and three of his children have just lost their lives in Switzerland, has occurred with such appalling suddenness that it is hard to realise that never again will he be seen in scientific circles.

By his death we lose not only an eminent electrician, mathematician, and engineer, but also a personal friend, whose energy, keen perception, and sound reasoning make the news of his untimely death the more startling.

Dr. Hopkinson was born in the year 1849, and received the first part of his education at Owens College, Manchester; in 1870 he took his degree as Doctor of Science at the London University. In the following year he took the Smith Prize, and attained the position of Senior Wrangler at Cambridge.

His work in electrical engineering is vast and well known; he has originated and carried out many schemes of electric traction and lighting, which will not allow his name to be forgotten.

He was the author of many works on scientific subjects, a member of the Board of Managers of the Royal Institution, a member of the Council of the British Association, twice President of the Institution of Electrical Engineers, besides belonging to other scientific societies.

UNIVERSITY COLLEGE, BRISTOL.
CHEMICAL DEPARTMENT.

Professor—SYDNEY YOUNG, D.Sc., F.R.S.
Lecturer—FRANCIS E. FRANCIS, B.Sc., Ph.D.
Demonstrator—D. H. JACKSON, M.A., B.Sc., Ph.D.

The SESSION 1898-99 begins on October 4th. Lectures on Inorganic, Organic, and Advanced Chemistry will be delivered during the Session. The Laboratories are fitted with the most recent improvements for the study of Practical Chemistry in all its branches. In the Evening the Laboratory is opened and Lectures on Inorganic Chemistry, at reduced fees, are delivered. Several Scholarships are tenable at the College.

CALENDAR, containing full information, price 1s. (by post 1s. 4d.).

For prospectus and further particulars apply to—
JAMES RAFTER, Secretary.

MASON UNIVERSITY COLLEGE, BIRMINGHAM.

FACULTIES OF ARTS AND SCIENCE.

SESSION 1898-99.

THE NEXT SESSION COMMENCES ON TUESDAY, OCTOBER 4.

COMPLETE COURSES OF INSTRUCTION are provided for the various Examinations in Arts and Science, and the Preliminary Scientific (M.B.) Examination of the University of London; for Students of Civil, Mechanical, and Electrical Engineering; and for those who desire to obtain an acquaintance with some branch of Applied Science, including Chemistry, Metallurgy, &c. Students may, however, attend any class or combination of classes.

There is also a Faculty of Medicine, a Syllabus of which containing full particulars may be had gratis from Messrs. Cornish, New Street.

A SYLLABUS of the Arts and Science Faculties, with full information as to the various lecture and laboratory courses, lecture days and hours, fees, entrance and other ssholarships, prizes, &c., may be had gratis from Messrs. Cornish, New Street, Birmingham; or on application to the Registrar, at the College.

CHEMISTRY AND PHYSICS.—For all Examinations, Practical and Theoretical. Well equipped Laboratory. Classes and Private Tuition; also Correspondence.—Evans, 9, Heathcote Street, Gray's Inn Road.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2024.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Bristol, 1898.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir William Crookes, F.R.S., V.P.C.S.

For the third time in its history the British Association meets in your City of Bristol. The first meeting was held under the presidency of the Marquis of Lansdowne in 1836, the second under the presidency of Sir John Hawkshaw in 1875. Formerly the President unrolled to the meeting a panorama of the year's progress in physical and biological sciences. To-day the President usually restricts himself to specialities connected with his own work or deals with questions which for the time are uppermost. To be President of the British Association is undoubtedly a great honour. It is also a great opportunity and a great responsibility; for I know that, on the wings of the Press, my words, be they worthy or not, will be carried to all points of the compass. I propose first to deal with the important question of the supply of bread to the inhabitants of these Islands, then to touch on subjects to which my life work has been more or less devoted. I shall not attempt any general survey of the sciences; these so far as the progress in them demands attention will be more fitly brought before you in the different sections either in the Addresses of the Presidents or in communications from Members.

Before proceeding with my address I wish to refer to the severe loss the British Association has sustained in the death of Lord Playfair. With Sir John Lubbock and Lord Rayleigh, Lord Playfair was one of the Permanent Trustees of our Association, and for many years he was present at our meetings. It would be difficult to overrate his loss to British science. Lord Playfair's well-matured and accurate judgment, his scientific knowledge, and his happy gift of clothing weighty thoughts in persuasive language, made his presence acceptable, whether in the council chamber, in departmental enquiries, or at light social gatherings, where, by the singular laws of modern society, momentous announcements are sometimes first given to the world. Lord Playfair (then Sir Lyon Playfair) was President of the British Association at Aberdeen in 1885; his Address on that occasion will long be remembered as a model of profound learning and luminous exposition.

And now I owe a sort of apology to this brilliant audience. I must ask you to bear with me for ten minutes, for I am afraid what I now have to say will prove somewhat dull. I ought to propitiate you, for to tell the truth, I am bound to bore you with figures. Statistics are rarely attractive to a listening audience; but they are necessary evils, and those of this evening are unusually doleful. Nevertheless when we have proceeded a little way on our journey I hope you will see that the river of figures is not hopelessly dreary. The stream leads into an almost unexplored region, and to the right and left we see channels opening out, all worthy of exploration, and promising a rich reward to the statistic explorer who will trace them to their source,—a harvest, as Huxley expresses it, "immediately convertible into those things which the most sordidly practical of men will admit to have value, namely, money and life." My chief subject is of interest to the whole world—to every race—to every human being. It is of urgent importance to-day, and it is a life and death question for generations to come. I mean the question of Food supply. Many of my statements you may think are of the alarmist order; certainly they are depressing, but they are founded on stubborn facts. They show that England and all civilised nations stand in deadly peril of not having enough to eat. As mouths multiply, food resources dwindle. Land is a limited quantity, and the land that will grow wheat is absolutely dependent on difficult and capricious natural phenomena. I am constrained to show that our wheat-producing soil is totally unequal to the strain put upon it. After wearying you with a survey of the universal dearth to be expected, I hope to point a way out of the colossal dilemma. It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty.

The food supply of the kingdom is of peculiar interest to this meeting, considering that the grain trade has always been, and still is, an important feature in the imports of Bristol. The imports of grain to this city amount to about 25 million bushels per annum—eight millions of which consist of wheat.

What are our home requirements in the way of wheat? The consumption of wheat per head of the population (unit consumption) is over 6 bushels per annum; and taking the population at 40 millions, we require no less than 240 million bushels of wheat, increasing annually by two million bushels to supply the increase of population. Of the total amount of wheat consumed in the United Kingdom we grow 25 and import 75 per cent.

So important is the question of wheat supply that it has attracted the attention of Parliament, and the question of national granaries has been mooted. It is certain that, in case of war with any of the great Powers, wheat would be contraband, as if it were cannon or powder, liable to capture, even under a neutral flag. We must therefore accept the situation and treat wheat as munitions of war and grow, accumulate, or store it as such. It has been shown that at the best, our stock of wheat and flour amounts only to 64,000,000 bushels—fourteen weeks' supply—while last April our stock was equal to only 10,000,000 bushels, the smallest ever recorded by "Beerbohm" for the period of the season. Similarly, the stocks held in Europe, the United States, and Canada, called "the world's visible supply," amounted to only 54,000,000 bushels, or ten millions less than last year's sum total, and nearly 82 millions less than that of 1893 or 1894 at the corresponding period. To arrest this impending danger, it has been proposed that an amount of 64,000,000 bushels of wheat should be purchased by the State and stored in national granaries, not to be opened, except to remedy deterioration of grain, or in view of national disaster rendering starvation imminent. This 64 million bushels would add another fourteen weeks' life to the population; assuming that the ordinary stock had not been drawn on, the wheat in the country would only then be enough to feed the population for twenty-eight weeks.

I do not venture to speak authoritatively on national granaries. The subject has been discussed in the daily press, and the recently published Report from the Agricultural Committee on National Wheat Stores brings together all the arguments in favour of this important scheme, together with the difficulties to be faced if it be carried out with necessary completeness.

More hopeful, although difficult and costly, would be the alternative of growing most, if not all of our own wheat supply here at home in the British Isles. The average yield over the United Kingdom last year was 29·07 bushels per acre; the average for the last eleven years being 29·46. For twelve months we need 240,000,000 bushels of wheat, requiring about 8¼ million acres of good wheat-growing land, or nearly 13,000

square miles, increasing at the rate of 100 square miles per annum, to render us self-supporting as to bread food. This area is about one-fourth the size of England.*

A total area of land in the United Kingdom equal to a plot 110 miles square, of quality and climate sufficient to grow wheat to the extent of 29 bushels per acre, does not seem a hopeless demand.† It is doubtful, however, if this amount of land could be kept under wheat, and the necessary expense of high farming faced, except under the imperious pressure of impending starvation, or the stimulus of a national subsidy or permanent high prices. Certainly these 13,000 square miles would not be available under ordinary economic conditions, for much, perhaps all the land now under barley and oats would not be suitable for wheat. In any case, owing to our cold, damp climate and capricious weather, the wheat crop is hazardous, and for the present, our annual deficit of 180,000,000 bushels must be imported. A permanently higher price for wheat is, I fear, a calamity that ere long must be faced. At enhanced prices, land now under wheat will be better farmed, and therefore will yield better, thus giving increased production without increased area.

The burning question of to-day is what can the United Kingdom do to be reasonably safe from starvation in presence of two successive failures of the world's wheat harvest, or against a hostile combination of European nations. We eagerly spend millions to protect our coasts and commerce; and millions more on ships, explosives, guns, and men; but we omit to take necessary precautions to supply ourselves with the very first and supremely important munition of war—food.

To take up the question of food-supply in its scientific aspect, I must not confine myself exclusively to our own national requirements. The problem is not restricted to the British Isles—the Bread-eaters of the whole world share the perilous prospect—and I do not think it out of place if on this occasion I ask you to take with me a wide general survey of the wheat supply of the whole world.

Wheat is the most sustaining food grain of the great Caucasian race, which includes the peoples of Europe, the United States, British America, the white inhabitants of South Africa, Australasia, parts of South America, and the white population of the European Colonies. Of late years the individual consumption of wheat has almost universally increased. In Scandinavia it has risen 100 per cent in twenty-five years; in Austro-Hungary, 80 per cent; in France, 20 per cent; while in Belgium it has increased 50 per cent. Only in Russia and Italy, and possibly Turkey, has the consumption of wheat per head declined.

In 1871 the bread-eaters of the world numbered 371,000,000. In 1881 the numbers rose to 416,000,000, in 1891 to 472,600,000, and at the present time they number 516,500,000. The augmentation of the world's bread-eating population in a geometrical ratio is evidenced by the fact that the yearly aggregates grow progressively larger. In the early seventies they rose 4,300,000 per annum, while in the eighties they increased by more than 6,000,000 per annum, necessitating annual additions to the bread supply nearly one-half greater than sufficed twenty-five years ago.

How much wheat will be required to supply all these hungry mouths with bread? At the present moment it is not possible to get accurate estimates of this year's wheat crops of the world, but an adequate idea may be gained from the realised crops of some countries and the promise of others. To supply 516,500,000 bread-eaters, if each bread-eating unit is to have his usual ration, will require a total of 2,324,000,000 bushels for seed and food. What are our prospects of obtaining this amount?

According to the best authorities the total supplies from the 1897-98 harvest are 1,921,000,000 bushels.* The requirement of the 516,500,000 bread-eaters for seed and food are 2,324,000,000 bushels; there is thus a deficit of 403,000,000 bushels, which has not been urgently apparent owing to a surplus of 300,000,000 bushels carried over from the last harvest. Respecting the prospects of the harvest year just beginning it must be borne in mind that there are no remainders to bring over from last harvest; we start with a deficit of 103,000,000 bushels and have 6,500,000 more mouths to feed. It follows, therefore, that one-sixth of the required bread will be lacking unless larger drafts than now seem possible can be made upon early produce from the next harvest.†

The majority of the wheat crops between 1882 and 1896 were in excess of current needs, and thus considerable reserves of wheat were available for supplementing small deficits from the four deficient harvests. But bread-eaters have almost eaten up the reserves of wheat, and the 1897 harvest being under average, the conditions become serious.‡ That scarcity and high prices have not prevailed in recent years is due to the fact that since 1889 we have had seven world crops of wheat and six of rye abundantly in excess of the average. These generous crops increased accumulations to such an extent as to obscure the fact that the harvests of 1895 and 1896 were each much below current requirements. Practically speaking, reserves are now exhausted, and bread-eaters must be fed from current harvests—accumulation under present conditions being almost impossible. This is obvious from the fact that a harvest equal to that of 1894 (the greatest crop on record, both in acre-yield and in the aggregate) would yield less than current needs.§

It is clear we are confronted with a colossal problem that must tax the wits of the wisest. When the bread-eaters have exhausted all possible supplies from the 1897-98 harvest, there will be a deficit of 103,000,000 bushels of wheat, with no substitution possible unless Europeans can be induced to eat Indian corn or rye bread. Up to recent years the growth of wheat has kept pace with demands. As wheat-eaters increased, the acreage under wheat expanded. The world has become so familiarised with the orderly sequence of demand and supply, so accustomed to look upon the vast plains of other wheat-growing countries as inexhaustible granaries, that in a light-hearted way it is taken for granted that so many million additional acres can be added year after year to the wheat-growing area of the world. We forget that the wheat-growing area is of strictly limited extent, and that a few million acres regularly absorbed soon mount to a formidable number.

The present position being so gloomy, let us consider future prospects. What are the capabilities as regards available area, economic conditions, and acreage yield of the wheat-growing countries from whence we now draw our supply?

For the last thirty years the United States have been the dominant factor in the foreign supply of wheat, exporting no less than 145,000,000 bushels. This shows how the bread-eating world has depended, and still depends, on the United States for the means of subsistence. The entire world's contributions to the food-bearing area have averaged but 4,000,000 acres yearly since 1869. It is scarcely possible that such an average, under existing conditions, can be doubled for the coming twenty-five years.‖ Almost yearly, since 1885, additions to the wheat-growing area have diminished, while the requirements of the increasing population of the States have advanced, so that the needed American supplies have been drawn from the acreage hitherto used for exportation. Practically there remains no uncultivated prairie land in the United States suitable for wheat-growing. The virgin

* Appendix A.
† The total area of the United Kingdom is 120,979 square miles; therefore the required land is about a tenth part of the total.

* Appendix B.
† Appendix C.
‡ Appendix D.
§ Appendix E.
‖ Appendix F.

land has been rapidly absorbed, until at present there is no land left for wheat without reducing the area for maize, hay, and other necessary crops.*

It is almost certain that within a generation the ever increasing population of the United States will consume all the wheat grown within its borders, and will be driven to import, and, like ourselves, will scramble for a lion's share of the wheat crop of the world. This being the outlook, exports of wheat from the United States are only of present interest and will gradually diminish to a vanishing point. The enquiry may be restricted to such countries as probably will continue to feed bread-eaters who annually derive a considerable part of their wheat from extraneous sources.

But if the United States, which grow about one-fifth of the world's wheat and contribute one-third of all wheat exportations, are even now dropping out of the race, and likely soon to enter the list of wheat-importing countries, what prospect is there that other wheat-growing countries will be able to fill the gap, and, by enlarging their acreage under wheat, replace the supply which the States have so long contributed to the world's food? The withdrawal of 145 million bushels will cause a serious gap in the food supply of wheat-importing countries, and unless this deficit can be met by increased supplies from other countries, there will be a dearth for the rest of the world after the British Isles are sufficiently supplied.

Next to the United States, Russia is the greatest wheat exporter, supplying nearly 95 million bushels.†

Although Russia at present exports so lavishly, this excess is merely provisional and precarious. The Russian peasant population increases more rapidly than any other in Europe. The yield per acre over European Russia is meagre—not more than 8·6 bushels to the acre—while some authorities consider it as low as 4·6 bushels. The cost of production is low—lower even than on the virgin soils of the United States. The development of the fertile though somewhat over-rated "black earth" which extends across the southern portion of the empire and beyond the Ural Mountains into Siberia progresses rapidly. But, as we have indicated, the consumption of bread in Russia has been reduced to danger point. The peasants starve and fall victims to "hunger typhus," whilst the wheat-growers export grain that ought to be consumed at home.

Considering Siberia as a wheat grower, climate is the first consideration. Summers are short—as they are in all regions with Continental climates north of the 45th parallel,—and the ripening of wheat requires a temperature averaging at least 65° F. for fifty-five to sixty-five days. As all Siberia lies north of the summer isotherm of 65°, it follows that such region is ill adapted to wheat culture unless some compensating climatic condition exists. As a fact, the conditions are exceptionally unfavourable in all but very limited districts in the two westernmost governments. The cultivable lands of Western Siberia adapted to grain bearing neither equal in extent nor in potential productive powers those of Iowa, Minnesota, and Nebraska. There are limited tracts of fair productiveness in Central Siberia and in the valleys of the southern affluents of the Amoor, but these are only just capable of supporting a meagre population.

Prince Hilkoff, Russian Minister of Ways and Communications, declared in 1896 that "Siberia never had produced, and never would produce, wheat and rye enough to feed the Siberian population." And, a year later, Prince Krapotkin backed the statement as substantially correct.

Those who attended the meeting of the British Association last year in Canada must have been struck with the extent and marvellous capacity of the fertile plains of Manitoba and the North-West Provinces. Here were to be seen 1,290,000 acres of fine wheat-growing land, yielding 18,261,950 bushels, one-fifth of which comes to hungry England. Expectations have been cherished that the Canadian North-West would easily supply the world with wheat, and exaggerated estimates are drawn as to the amount of surplus land on which wheat can be grown.* Thus far, performance has lagged behind promise, the wheat-bearing area of all Canada having increased less than 500,000 acres since 1884, while the exports have not increased in greater proportion. As the wheat area of Manitoba and the North-West has increased, the wheat area of Ontario and the Eastern provinces has decreased; the added acres being little more than sufficient to meet the growing requirements of population. We have seen calculations showing that Canada contains 500,000,000 acres of profitable wheat land. The impossibility of such an estimate ever being fulfilled will be apparent when it is remembered that the whole area employed in both temperate zones for growing all the staple food crops is not more than 580,000,000 acres, and that in no country has more than 9 per cent of the area been devoted to wheat culture.†

The fertility of the North-West Provinces of the Dominion is due to an exceptional and curious circumstance. In winter the ground freezes to a considerable depth. Wheat is sown in the spring, generally April, when the frozen ground has been thawed to a depth of three inches. Under the hot sun of the short summer the grain sprouts with surprising rapidity, partly because the roots are supplied with water from the thawing depths. The summer is too short to thaw the ground thoroughly, and gate-posts or other dead wood extracted in autumn are found still frozen at their lower ends.

Australasia as a potential contributor to the world's supply of wheat affords another fertile field for speculation. Climatic conditions limit the Australian wheat area to a small portion of the southern littoral belt. Professor Shelton considers there are still fifty million acres in Queensland suitable for wheat, but hitherto it has never had more than 150,000 acres under cultivation. Crops in former days were liable to rust, but since the Rust in Wheat conferences and the dissemination of instruction to farmers, rust no longer has any terrors. I am informed by the Queensland Department of Agriculture that of late years they practically have bred wheat vigorous enough to resist this plague. For the second season in succession the wheat crop last year was destroyed over large areas in Victoria; and in South Australia the harvest averaged not more than about 3¾ bushels per acre, after meeting Colonial requirements for food and seed, leaving only 684,000 bushels for export. In most other districts the yield fails to such an extent as to cause Europeans to wonder why the pursuit of wheat raising is continued.

New Zealand has a moist climate resembling that of central and southern England, while South Australia is semi-arid, resembling western Kansas. Only two countries in the world yield as much wheat per acre as New Zealand—these are Denmark and the United Kingdom. Notwithstanding the great yield of wheat due to an equable climate, New Zealand finds fruit and dairy farming still more profitable. The climatic conditions favourable to wheat are also conducive to luxuriant growths of nutritious grasses. Thus the New Zealander ships his butter more than half-way round the world and competes successfully with western Europe.

During the last twenty-seven years the Austro-Hungarian population has increased 21·8 per cent as against an increase of 54·6 per cent in the acreage of wheat. Notwithstanding this disparity in the rates of increase, exports have practically ceased by reason of an advance of nearly 80 per cent in unit-consumption. There can be little doubt that Austro-Hungary is about to enter the ranks of importing nations, although in Hungary a con-

* Appendix G.
† Appendix H.

* Appendix I.
† Appendix J.

siderable area of wheat land remains to be brought under cultivation.*

Rumania is an important wheat-growing country. In 1896 it produced 69,000,000 bushels, and exported 34,000,000 bushels. It has a considerable amount of surplus land which can be used for wheat, although for many years the wheat area is not likely to exceed home requirements.

As a producer of wheat France comes next to the United States, but for our purpose she counts but little, being dependent on supplies from abroad for an average quantity of 14 per cent of her own production. There is practically no spare land in France that can be put under wheat in sufficient quantity to enable her to do more than provide for increase of population..

Germany is a gigantic importer of wheat, her imports rising 700 per cent in the last twenty-five years, and now averaging 35,000,000 bushels. Other nations of Europe also importers do not require detailed mention, as under no conceivable conditions would they be able to do more than supply wheat for the increasing requirements of their local population, and, instead of replenishing, would probably diminish, the world's stores.

The prospective supply of wheat from Argentina and Uruguay has been greatly over-rated. The agricultural area includes less than 100,000,000 acres of good, bad, and indifferent lands, much of which is best adapted for pastoral purposes. There is no prospect of Argentina ever being able to devote more than 30,000,000 acres to wheat; the present wheat area is about 6,000,000 acres, an area that may be doubled in the next twelve years. But the whole arable region is subject to great climatic vicissitudes, and to frosts that ravage the fields south of the 37th parallel. Years of systematised energy are frustrated in a few days —perhaps hours—by a single cruelty of Nature, such as a plague of locusts, a tropical rain, or a devastating hail storm. It will take years to bring the surplus lands of Argentina into cultivation, and the population is even now insufficient to supply labour at seed time and harvest.

During the next twelve years, Uruguay may add a million acres to the world's wheat fields; but social, political, and economic conditions seriously interfere with agricultural development.

At the present time South Africa is an importer of wheat, and the regions suitable to cereals do not exceed a few million acres. Great expectations have been formed as to the fertility of Mashonaland, the Shire Highlands, and the Kikuyu plateau, and as to the adaptation of these regions to the growth of wheat. But wheat culture fails where the banana ripens, and the banana flourishes throughout central Africa, except in limited areas of great elevation. In many parts of Africa insect pests render it impossible to store grain, and without grain stores there can be little hope of large exports.

North Africa, formerly the granary of Rome, now exports less than 5,000,000 bushels of wheat annually, and these exports are on the decline owing to increased home demands. With scientific irrigation, Egypt could supply three times her present amount of wheat, although no increase is likely unless the cotton fields of the Delta are diverted to grain growing. In Algeria and Tunis nearly all reclaimed lands are devoted to the production of wine, for which a brisk demand exists. Were this land devoted to the growth of wheat an additional five million bushels might be obtained.

The enormous acreage devoted to wheat in India has been declining for some years, and in 1895 over 20,000,000 acres yielded 185,000,000 bushels. Seven-eighths of this harvest is required for native consumption, and only one-eighth on an average is available for export. The annual increase of population is more than 3,000,000, demanding an addition to the food-bearing lands of not less than 1,800,000 acres annually. In recent years the increase has been less than one-fourth of this amount.†

* Appendix K.
† Appendix L.

In surveying the limitations and vicissitudes of wheat crops I have endeavoured to keep free from exaggeration and have avoided insistance on doubtful points. I have done my best to get trustworthy facts and figures, but from the nature of the case it is impossible to attain complete accuracy. Great caution is required in sifting the numerous varying current statements respecting the estimated areas and total produce of wheat throughout the world. The more closely official estimates are examined the more defective are they found, and comparatively few figures are sufficiently well established to bear the deductions often drawn. In doubtful cases I have applied to the highest authorities in each country, and in the case of conflicting accounts have taken data the least favourable to sensational or panic-engendering statements. In a few instances of accurate statistics their value is impaired by age; but for 95 per cent of my figures I quote good authorities, while for the remaining 5 per cent I rely on the best commercial estimates derived from the appearance of the growing crops, the acreage under cultivation, and the yield last year. The maximum probable error would make no appreciable difference in my argument.

The facts and figures I have set before you are easily interpreted. Since 1871, unit consumption of wheat, including seed, has slowly increased in the United Kingdom to the present amount of 6 bushels per head per annum; while the rate of consumption for seed and food by the whole world of bread-eaters was 4·15 bushels per unit per annum for the eight years ending 1878 and at the present time is 4·5 bushels. Under present conditions of low acre yield, wheat cannot long retain its dominant position among the food-stuffs of the civilised world. The details of the impending catastrophe no one can predict, but its general direction is obvious enough. Should all the wheat-growing countries add to their area to the utmost capacity, on the most careful calculation the yield would give us only an addition of some 100,000,000 acres, supplying at the average world-yield of 12·7 bushels to the acre, 1,270,000,000 bushels, just enough to supply the increase of population among bread-eaters till the year 1931.*

At the present time there exists a deficit in the wheat area of 31,000 square miles,—a deficit masked by the fact that the ten world crops of wheat harvested in the ten years ending 1896 were more than 5 per cent above the average of the previous twenty-six years.

When provision shall have been made, if possible, to feed 230,000,000 units likely to be added to the bread-eating populations by 1931,— by the complete occupancy of the arable areas of the temperate zone now partially occupied—where can be grown the additional 330,000,000 bushels of wheat required ten years later by a hungry world? What is to happen if the present rate of population be maintained, and if arable areas of sufficient extent cannot be adapted and made contributory to the subsistence of so great a host?

Are we to go hungry and to know the trial of scarcity? That is the poignant question. Thirty years is but a day in the life of a nation. Those present who may attend the meeting of the British Association thirty years hence will judge how far my forecasts are justified.

If bread fails not only us but all the bread-eaters of the world—what are we to do? We are born wheat-eaters. Other races, vastly superior to us in numbers, but differing widely in material and intellectual progress, are eaters of Indian corn, rice, millet, and other grains; but none of these grains have the food value, the concentrated health sustaining power of wheat, and it is on this account that the accumulated experience of civilised mankind has set wheat apart as the fit and proper food for the development of muscle and brains.

It is said that when other wheat-exporting countries realise that the states can no longer keep pace with the demand, these countries will extend their area of cultiva-

* Appendix M.

tion, and struggle to keep up the supply *pari passu* with the falling off in other quarters. But will this comfortable and cherished doctrine bear the test of examination?

Cheap production of wheat depends on a variety of causes, varying greatly in different countries. Taking the cost of producing a given quantity of wheat in the United Kingdom at 100*s.*, the cost for the same amount in the United States is 67*s.*, in India 66*s.*, and in Russia 54*s.* We require cheap labour, fertile soil, easy transportation to market, low taxation and rent, and no export or import duties. Labour will rise in price, and fertility diminish as the requisite manurial constituents in the virgin soil become exhausted. Facility of transportation to market will be aided by railways, but these are slow, and costly to construct, and it will not pay to carry wheat by rail beyond a certain distance. These considerations show that the price of wheat tends to increase. On the other hand, the artificial impediments of taxation and customs duties tend to diminish as demand increases and prices rise.

I have said that starvation may be averted through the laboratory. Before we are in the grip of actual dearth the Chemist will step in and postpone the day of famine to so distant a period that we, and our sons and grandsons, may legitimately live without undue solicitude for the future.

It is now recognised that all crops require what is called a "dominant" manure. Some need nitrogen, some potash, others phosphates. Wheat pre-eminently demands nitrogen, fixed in the form of ammonia or nitric acid. All other necessary constituents exist in the soil; but nitrogen is mainly of atmospheric origin, and is rendered "fixed" by a slow and precarious process which requires a combination of rare meteorological and geographical conditions to enable it to advance at a sufficiently rapid rate to become of commercial importance.

There are several sources of available nitrogen. The distillation of coal in the process of gas-making yields a certain amount of its nitrogen in the form of ammonia; and this product, as sulphate of ammonia, is a substance of considerable commercial value to gas companies. But the quantity produced is comparatively small; all Europe does not yield more than 400,000 annual tons, and, in view of the unlimited nitrogen required to substantially increase the world's wheat crop, this slight amount of coal ammonia is not of much significance. For a long time guano has been one of the most important sources of nitrogenous manures, but guano deposits are so near exhaustion that they may be dismissed from consideration.

Much has been said of late years, and many hopes raised by the discovery of Hellriegel and Wilfarth that leguminous plants bear on their roots nodosities abounding in bacteria endowed with the property of fixing atmospheric nitrogen; and it is proposed that the necessary amount of nitrogen demanded by grain crops should be supplied to the soil by cropping it with clover and ploughing in the plant when its nitrogen assimilisation is complete. But it is questionable whether such a mode of procedure will lead to the lucrative stimulation of crops. It must be admitted that practice has long been ahead of science, and for ages farmers have valued and cultivated leguminous crops. The four-course rotation is turnips, barley, clover, wheat,—a sequence popular more than two thousand years ago. On the Continent, in certain localities, there has been some extension of microbe cultivation; at home we have not reached even the experimental stage. Our present knowledge leads to the conclusion that the much more frequent growth of clover on the same land, even with successful microbe-seeding and proper mineral supplies, would be attended with uncertainty and difficulties. The land soon becomes what is called "clover sick" and turns barren.

There is still another and invaluable source of fixed nitrogen. I mean the treasure locked up in the sewage and drainage of our towns. Individually the amount so lost is trifling, but multiply the loss by the number of inhabitants, and we have the startling fact that, in the United Kingdom, we are content to hurry down our drains and water courses into the sea, fixed nitrogen to the value of no less than £16,000,000 per annum. This unspeakable waste continues, and no effective and universal method is yet contrived of converting sewage into corn. Of this barbaric waste of manurial constituents Liebig, nearly half a century ago, wrote in these prophetic words: —"Nothing will more certainly consummate the ruin of England than a scarcity of fertilisers—it means a scarcity of food. It is impossible that such a sinful violation of the divine laws of Nature should for ever remain unpunished; and the time will probably come for England sooner than for any other country, when, with all her wealth in gold, iron, and coal, she will be unable to buy one-thousandth part of the food which she has, during hundreds of years, thrown recklessly away."

The more widely this wasteful system is extended, recklessly returning to the sea what we have taken from the land, the more surely and quickly will the finite stocks of nitrogen locked up in the soils of the world become exhausted. Let us remember that the plant creates nothing; there is nothing in bread which is not absorbed from the soil, and unless the abstracted nitrogen is returned to the soil, its fertility must ultimately be exhausted. When we apply to the land nitrate of soda, sulphate of ammonia, or guano, we are drawing on the earth's capital, and our drafts will not perpetually be honoured. Already we see that a virgin soil cropped for several years loses its productive powers and without artificial aid becomes infertile. Thus the strain to meet demands is increasingly great. Witness the yield of 40 bushels of wheat per acre under favourable conditions, dwindling through exhaustion of soil to less than 7 bushels of poor grain, and the urgency of husbanding the limited store of fixed nitrogen becomes apparent. The store of nitrogen in the atmosphere is practically unlimited, but it is fixed and rendered assimilable by plants only by cosmic processes of extreme slowness. The nitrogen which with a light heart we liberate in a battleship broadside, has taken millions of minute organisms patiently working for centuries to win from the atmosphere.*

The only available compound containing sufficient fixed nitrogen to be used on a world-wide scale as a nitrogenous manure is nitrate of soda, or Chili saltpetre. This substance occurs native over a narrow band of the plain of Tamarugal, in the northern provinces of Chili between the Andes and the coast hills. In this rainless district for countless ages the continuous fixation of atmospheric nitrogen by the soil, its conversion into nitrate by the slow transformations of billions of nitrifying organisms, its combination with soda, and the crystallisation of the nitrate, have been steadily proceeding until the nitrate fields of Chili have become of vast commercial importance, and promise to be of inestimably greater value in the future. The growing exports of nitrate from Chili at present amount to about 1,200,000 tons.

The present acreage devoted to the world's growth of wheat is about 163,000,000 acres. At the average of 12·7 bushels per acre this gives 2,070,000,000 bushels. But thirty years hence the demand will be 3,260,000,000 bushels, and there will be difficulty in finding the necessary acreage on which to grow the additional amount required. By increasing the present yield per acre from 12·7 to 20 bushels we should with our present acreage secure a crop of the requisite amount. Now from 12·7 to 20 bushels per acre is a moderate increase of productiveness, and there is no doubt that a dressing with nitrate of soda will give this increase and more.

The action of nitrate of soda in improving the yield of wheat has been studied practically by Sir John Lawes and Sir Henry Gilbert on their experimental field at Rothamstead. This field was sown with wheat for thirteen con-

* Appendix N.

secutive years without manure, and yielded an average of 11·9 bushels to the acre. For the next thirteen years it was sown with wheat, and dressed with 5 cwt. of nitrate of soda per acre, other mineral constituents also being present. The average yield for these years was 36·4 bushels per acre—an increase of 24·5 bushels. In other words 22·86 lbs. of nitrate of soda produce an increase of one bushel of wheat.

At this rate, to increase the world's crop of wheat by 7·3 bushels, about 1¼ cwt. of nitrate of soda must annually be applied to each acre. The amount required to raise the world's crop on 163,000,000 acres from the present supply of 2,070,000,000 bushels to the required 3,260,000,000 bushels will be 12 million tons distributed in varying amounts over the wheat-growing countries of the world. The countries which produce more than the average of 12·7 bushels will require less, and those below the average will require more; but broadly speaking, about 12,000,000 tons annually of nitrate of soda will be required, in addition to the 1¼ million tons already absorbed by the world.

It is difficult to get trustworthy estimates of the amount of nitrate surviving in the nitre beds. Common rumour declares the supply to be inexhaustible, but cautious local authorities state that at the present rate of export, of over one million tons per annum, the raw material "caliche," containing from 25 to 50 per cent nitrate, will be exhausted in from twenty to thirty years.

Dr. Newton, who has spent years on the nitrate fields, tells me there is a lower class material containing a small proportion of nitrate which cannot at present be used, but which may ultimately be manufactured at a profit. Apart from a few of the more scientific manufacturers, no one is sanguine enough to think this debatable material will ever be worth working. If we assume a liberal estimate for nitrate obtained from the lower grade deposit, and say that it will equal in quantity that from the richer quality, the supply may last, possibly, fifty years, at the rate of a million tons a year; but at the rate required to augment the world's supply of wheat to the point demanded thirty years hence, it will not last more than four years.

I have passed in review all the wheat-growing countries of the world, with the exception of those whose united supplies are so small as to make little appreciable difference to the argument. The situation may be summed up briefly thus:—The world's demand for wheat—the leading bread-stuff—increases in a crescendo ratio year by year. Gradually all the wheat-bearing land on the globe is appropriated to wheat growing, until we are within measurable distance of using the last available acre. We must then rely on nitrogenous manures to increase the fertility of the land under wheat, so as to raise the yield from the world's low average—12·7 bushels per acre—to a higher average. To do this efficiently and feed the bread-eaters for a few years will exhaust all the available store of nitrate of soda. For years past we have been spending fixed nitrogen at a culpably extravagant rate, heedless of the fact that it is fixed with extreme slowness and difficulty, while its liberation in the free state takes place always with rapidity and sometimes with explosive violence.

Some years ago Mr. Stanley Jevons uttered a note of warning as to the near exhaustion of our British coal fields. But the exhaustion of the world's stock of fixed nitrogen is a matter of far greater importance. It means not only a catastrophe little short of starvation for the wheat-eaters, but indirectly, scarcity for those who exist on inferior grains, together with a lower standard of living for meat eaters, scarcity of mutton and beef, and even the extinction of gunpowder!

There is a gleam of light amid this darkness of despondency. In its free state nitrogen is one of the most abundant and pervading bodies on the face of the earth. Every square yard of the earth's surface has nitrogen gas pressing down on it to the extent of about 7 tons—but this is in the *free* state, and wheat demands it *fixed*. To convey this idea in an object-lesson, I may tell you that, previous to its destruction by fire, Colston Hall, measuring 146 feet by 80 feet by 70 feet, contained 27 tons weight of nitrogen in its atmosphere; it also contained one-third of a ton of argon. In the free gaseous state this nitrogen is worthless; combined in the form of nitrate of soda it would be worth about £2000.

For years past attempts have been made to effect the fixation of atmospheric nitrogen, and some of the processes have met with sufficient partial success to warrant experimentalists in pushing their trials still further; but I think I am right in saying that no process has yet been brought to the notice of scientific or commercial men which can be considered successful either as regards cost or yield of product. It is possible, by several methods, to fix a certain amount of atmospheric nitrogen; but to the best of my knowledge no process has hitherto converted more than a small amount, and this at a cost largely in excess of the present market value of fixed nitrogen.

The fixation of atmospheric nitrogen therefore is one of the great discoveries awaiting the ingenuity of chemists. It is certainly deeply important in its practical bearings on the future welfare and happiness of the civilised races of mankind. This unfulfilled problem, which so far has eluded the strenuous attempts of those who have tried to wrest the secret from nature, differs materially from other chemical discoveries which are in the air, so to speak, but are not yet matured. The fixation of nitrogen is vital to the progress of civilised humanity. Other discoveries minister to our increased intellectual comfort, luxury, or convenience; they serve to make life easier, to hasten the acquisition of wealth, or to save time, health, or worry. The fixation of nitrogen is a question of the not far distant future. Unless we can class it among certainties to come the great Caucasian race will cease to be foremost in the world, and will be squeezed out of existence by races to whom wheaten bread is not the staff of life.

Let me see if it is not possible even now to solve the momentous problem. As far back as 1892 I exhibited at one of the Soirées of the Royal Society an experiment on "The Flame of Burning Nitrogen." I showed that nitrogen is a combustible gas, and the reason why when once ignited the flame does not spread through the atmosphere and deluge the world in a sea of nitric acid is that its igniting point is higher than the temperature of its flame—not, therefore, hot enough to set fire to the adjacent mixture. But by passing a strong induction current between terminals the air takes fire and continues to burn with a powerful flame, producing nitrous and nitric acids. This inconsiderable experiment may not unlikely lead to the development of a mighty industry destined to solve the great food problem. With the object of burning out nitrogen from air so as to leave argon behind, Lord Rayleigh fitted up apparatus for performing the operation on a larger scale, and succeeded in effecting the union of 29·4 grms. of mixed nitrogen and oxygen at an expenditure of one-horse power. Following these figures it would require one Board of Trade unit to form 74 grms. of nitrate of soda, and therefore 14,000 units to form one ton. To generate electricity in the ordinary way with steam engines and dynamos, it is now possible with a steady load night and day, and engines working at maximum efficiency, to produce current at a cost of one-third of a penny per Board of Trade unit. At this rate one ton of nitrate of soda would cost £26. But electricity from coal and steam engines is too costly for large industrial purposes; at Niagara where water power is used, electricity can be sold at a profit for 1/17th of a penny per Board of Trade unit. At this rate nitrate of soda would cost not more than £5 per ton. But the limit of cost is not yet reached, and it must be remembered that the initial data are derived from small scale experiments, in which the object was not economy, but rather to demonstrate the practicability of the combustion method, and to utilise it for isolating argon. Even now electric nitrate at £5 a ton compares favourably with

Chili nitrate at £7 10s. a ton; and all experience shows that when the road has been pointed out by a small laboratory experiment the industrial operations that may follow are always conducted at a cost considerably lower than could be anticipated from the laboratory figures.

Before we decide that electric nitrate is a commercial possibility a final question must be mooted. We are dealing with wholesale figures, and must take care that we are not simply shifting difficulties a little further back without really diminishing them. We start with a shortage of wheat, and the natural remedy is to put more land under cultivation. As the land cannot be stretched and there is so much of it and no more, the object is to render the available area more productive by a dressing with nitrate of soda. But nitrate of soda is limited in quantity, and will soon be exhausted. Human ingenuity can contend even with these apparently hopeless difficulties. Nitrate can be produced artificially by the combustion of the atmosphere. Here we come to finality in one direction, our stores are inexhaustible. But how about electricity? Can we generate enough energy to produce 12,000,000 tons of nitrate of soda annually. A preliminary calculation shows that there need be no fear on that score; Niagara alone is capable of supplying the required electric energy without much lessening its mighty flow.

The future can take care of itself. The artificial production of nitrate is clearly within view, and by its aid the land devoted to wheat can be brought up to the 30 bushels per acre standard. In days to come, when the demand may again overtake supply, we may safely leave our successors to grapple with the stupendous food problem.

And in the next generation instead of trusting mainly to food-stuffs which flourish in temperate climates, we probably shall trust more and more to the exuberant food-stuffs of the tropics, where, instead of one yearly sober harvest, jeopardised by any shrinkage of the scanty days of summer weather, or of the few steady inches of rainfall, Nature annually supplies heat and water enough to ripen two or three successive crops of food-stuffs in extraordinary abundance. To mention one plant alone, Humboldt—from what precise statistics I know not—computed that, acre for acre, the food-productiveness of the banana is 133 times that of wheat—the unripe banana, before its starch is converted into sugar, is said to make excellent bread.

Considerations like these must in the end determine the range and avenues of commerce, perhaps the fate of continents. We must develope and guide Nature's latent energies, we must utilise her inmost workshops, we must call into commercial existence Central Africa and Brazil to redress the balance of Odessa and Chicago.

Having kept you for the last half-hour rigorously chained to earth, disclosing dreary possibilities, it will be a relief to soar to the heights of pure Science and to discuss a point or two touching its latest achievements and aspirations. The low temperature researches which bring such renown to Professor Dewar and to his laboratory in the Royal Institution, have been crowned during the present year by the conquest of one of Nature's most defiant strongholds. On the 10th of last May Professor Dewar wrote to me these simple but victorious words—"This evening I have succeeded in liquefying both hydrogen and helium. The second stage of low temperature work has begun." Static hydrogen boils at a temperature of $-238°$ C. at ordinary pressure, and at $-250°$ C. in a vacuum, thus enabling us to get within 23° C. of absolute zero. The density of liquid hydrogen is only 1/14th that of water, yet in spite of such a low density it collects well, drops easily, and has a well-defined meniscus. With proper isolation it will be as easy to manipulate liquid hydrogen as liquid air.

The investigation of the properties of bodies brought near the absolute zero of temperature is certain to give results of extraordinary importance. Already platinum resistance thermometers are becoming useless, as the temperature of boiling hydrogen is but a few degrees from the point where the resistance of platinum would be practically nothing, or the conductivity infinite.

Several years ago I pondered on the constitution of matter in what I ventured to call the fourth state. I endeavoured to probe the tormenting mystery of the atom. What *is* the atom? Is a single atom in space solid, liquid, or gaseous? Each of these states involves ideas which can only pertain to vast collections of atoms. Whether like Newton, we try to visualise an atom as a hard spherical body, or with Boscovitch and Faraday, to regard it as a centre of force, or accept the vortex atom theory of Lord Kelvin, an isolated atom is an unknown entity difficult to conceive. The properties of matter—solid, liquid, gaseous—are due to molecules in a state of motion. Therefore, Matter as we know it involves essentially a mode of motion; and the atom itself—intangible, invisible, and inconceivable—is its material basis, and may, indeed, be styled the only true *matter*. The space involved in the motions of atoms has no more pretension to be called matter than the sphere of influence of a body of riflemen—the sphere filled with flying leaden missiles—has to be called lead. Since what we call Matter essentially involves a mode of motion, and since at the temperature of absolute zero all atomic motions would stop, it follows that matter as we know it would at that paralysing temperature probably entirely change its properties. Although a discussion of the ultimate absolute properties of matter is purely speculative, it can hardly be barren, considering that in our laboratories we are now within moderate distance of the absolute zero of temperature.

I have dwelt on the value and importance of nitrogen, but I must not omit to bring to your notice those little known and curiously related elements which during the past twelve months have been discovered and partly described by Professor Ramsay and Dr. Travers. For many years my own work has been among what I may call the waste heaps of the mineral elements. Professor Ramsay is dealing with vagrant atoms of an astral nature. During the course of the present year he has announced the existence of no fewer than three new gases—krypton, neon, and metargon. Whether these gases, chiefly known by their spectra, are true unalterable elements, or whether they are compounded of other known or unknown bodies, has yet to be proved. Fellow workers freely pay tribute to the painstaking zeal with which Professor Ramsay has conducted a difficult research, and to the philosophic subtlety brought to bear on his investigations. But, like most discoverers, he has not escaped the flail of severe criticism.

There is still another claimant for celestial honours. Professor Nasini tells us he has discovered, in some volcanic gases at Pozzuoli, that hypothetical element Coronium, supposed to cause the bright line 5316·9 in the spectrum of the sun's corona. Analogy points to its being lighter and more diffusible than hydrogen, and a study of its properties cannot fail to yield striking results. Still awaiting discovery by the fortunate spectroscopist are the unknown celestial elements Aurorium, with a characteristic line at 5570·7—and Nebulum, having two bright lines at 5007·05 and 4959·02.

The fundamental discovery by Hertz, of the electromagnetic waves predicted more than thirty years ago by Clerk Maxwell, seems likely to develop in the direction of a practical application which excites keen interest;—I mean the application to electric signalling across moderate distances without connecting wires. The feasibility of this method of signalling has been demonstrated by several experimenters at more than one meeting of the British Association, though most elaborately and with many optical refinements by Oliver Lodge at the Oxford meeting in 1894. But not until Signor Marconi induced the British Post-Office and Foreign Governments to try large scale experiments did wireless signalling become generally

and popularly known or practically developed as a special kind of telegraphy. Its feasibility depends on the discovery of a singularly sensitive detector for Hertz waves,—a detector whose sensitiveness in some cases seems almost to compare with that of the eye itself. The fact noticed by Oliver Lodge in 1889, that an infinitesimal metallic gap subjected to an electric jerk became conducting, so as to complete an electric circuit, was re-discovered soon afterwards in a more tangible and definite form and applied to the detection of Hertz waves by M. E. Branly. Oliver Lodge then continued the work and produced the *vacuum filing-tube* coherers with automatic tapperback which are of acknowledged practical service. It is this varying continuity of contact under the influence of extremely feeble electric stimulus alternating with mechanical tremor, which, in combination with the mode of producing the waves revealed by Hertz, constitutes the essential and fundamental feature of "wireless telegraphy." There is a curious and widely spread misapprehension about coherers to the effect that to make a coherer work the wave must fall upon it. Oliver Lodge has disproved this fallacy. Let the wave fall on a suitable receiver, such as a metallic wire, or, better still, on an arrangement of metal wings resembling a Hertz sender, and the waves set up oscillating currents which may be led by wires (enclosed in metal pipes) to the coherer. The coherer acts apparently by a species of end-impact of the oscillatory current, and does not need to be attacked in the flank by the waves themselves. This interesting method of signalling — already developing in Marconi's hands into a successful practical system which inevitably will be largely used in lighthouse and marine work — presents more analogy to optical signals by flash-light than to what is usually understood as electric telegraphy; notwithstanding the fact that an ordinary Morse instrument at one end responds to the movements of a key at the other, or, as arranged by Alexander Muirhead, a siphon recorder responds to an automatic transmitter at about the rate of slow cable telegraphy. But although no apparent optical apparatus is employed, it remains true that the impulse travels from sender to receiver by essentially the same process as that which enables a flash of magnesium powder to excite a distant eye.

The phenomenon discovered by Zeeman, that a source of radiation is affected by a strong magnetic field in such a way that light of one refrangibility becomes divided usually into three components, two of which are displaced by diffraction analysis on either side of the mean position and are oppositely polarised to the third or residual constituent, has been examined by many observers in all countries. The phenomenon has been subjected to photography with conspicuously successful results by Professor T. Preston in Dublin and by Professor Michelson and Dr. Ames and others in America.

It appears that the different lines in the spectrum are differently affected, some of them being tripled with different grades of relative intensity, some doubled, some quadrupled, some sextupled, and some left unchanged. Even the two components of the D lines are not similarly influenced. Moreover, whereas the polarisation is usually such as to indicate that motions of a negative ion or electron constitute the source of light, a few lines are stated by the observers at Baltimore, who use what they call the "small" grating of 5 inches width ruled with 65,000 lines, to be polarised in the reverse way.

Further prosecution of these researches must lead to deeper insight into molecular processes and the mode in which they affect the ether; indeed already valuable theoretic views have been promulgated by H. A. Lorentz, J. Larmor, and G. F. Fitzgerald, on the lines of the radiation theory of Dr. Johnstone Stoney; and the connection of the new phenomena with the old magnetic rotation of Faraday is under discussion. It is interesting to note that Faraday and a number of more recent experimenters were led by theoretical considerations to look for some such effect; and though the inadequate means at their disposal did not lead to success, nevertheless a first dim glimpse of the phenomenon was obtained by M. Fievez, of the Royal Observatory at Brussels, in 1885.

It would be improper to pass without at least brief mention, the remarkable series of theoretic papers by Dr. J. Larmor, published by the Royal Society, on the relationship between ether and matter. By the time these researches become generally intelligible they may be found to constitute a considerable step towards the further mathematical analysis and interpretation of the physical universe on the lines initiated by Newton.

In the mechanical construction of Röntgen ray tubes I can record a few advances: the most successful being the adoption of Professor Silvanus P. Thompson's suggestion of using for the anti-cathode a metal of high atomic weight. Osmium and iridium have been used with advantage, and osmium anticathode tubes are now a regular article of manufacture. As long ago as June, 1896, X-ray tubes with metallic uranium anticathodes were made in my own laboratory, and were found to work better than those with platinum. The difficulty of procuring metallic uranium prevented these experiments from being continued. Thorium anticathodes have also been tried.

Röntgen has drawn fresh attention to a fact very early observed by English experimenters — that of the non-homogeneity of the rays and the dependence of their penetrating power on the degree of vacuum; rays generated in high vacua have more penetrative power than when the vacuum is less high. These facts are familiar to all who have exhausted focus tubes on their own pumps. Röntgen suggests a convenient phraseology; he calls a low vacuum tube, which does not emit the highly penetrating rays, a "soft" tube, and a tube in which the exhaustion has been pushed to an extreme degree, in which highly penetrating rays predominate, a "hard" tube. Using a "hard" tube he took a photograph of a double-barrelled rifle, and showed not only the leaden bullets within the steel barrels but even the wads and the charges.

Benoit has re-examinnd the alleged relation between density and opacity to the rays, and finds certain discrepancies. Thus, the opacity of equal thicknesses of palladium and platinum are nearly equal whilst their densities and atomic weights are very different, those of palladium being about half those of platinum.

At the last meeting of the British Association visitors saw — at the McGill University — Professors Cox and Callendar's apparatus for measuring the velocity of Röntgen rays. They found it to be certainly greater than 200 kilometres per second. Majorana has made an independent determination, and finds the velocity to be 600 kilometres per second with an inferior limit certainly of not less than 150 kilometres per second. It may be remembered that J. J. Thomson has found for cathode rays a velocity of more than 10,000 kilometres per second, and it is extremely unlikely that the velocity of Röntgen rays will prove to be less.

Trowbridge has verified the fact, previously announced by Professor S. P. Thompson, that fluor-spar, which by prolonged heating has lost its power of luminescing when re-heated, regains the power of thermo-luminescence when exposed to Röntgen rays. He finds that this restoration is also effected by exposure to the electric glow discharge, but not by exposure to ultra-violet light. The difference is suggestive.

As for the action of Röntgen rays on bacteria, often asserted and often denied, the latest statement by Dr. H. Rieder, of Munich, is to the effect that bacteria are killed by the discharge from "hard" tubes. Whether the observation will lead to results of pathologic importance remains to be seen. The circumstance that the normal retina of the eye is slightly sensitive to the rays is confirmed by Dorn and by Röntgen himself.

The essential wave-nature of the Röntgen rays appears to be confirmed by the fact ascertained by several of our great mathematical physicists, that light of excessively

short wave-length would be but slightly absorbed by ordinary material media, and would not in the ordinary sense be refracted at all. In fact a theoretic basis for a comprehension of the Röntgen rays had been propounded before the rays were discovered. At the Liverpool meeting of the British Association, several speakers, headed by Sir George Stokes, expressed their conviction that the disturbed electric field caused by the sudden stoppage of the motion of an electrically charged atom yielded the true explanation of the phenomena extraneous to the Crookes high vacuum tubes,—phenomena so excellently elaborated by Lenard and by Röntgen. More recently Sir George Stokes has re-stated his "pulse" theory and fortified it with arguments which have an important bearing on the whole theory of the refraction of light. He still holds to their essentially transverse nature, in spite of the absence of polarisation, an absence once more confirmed by the careful experiments of Dr. L. Graetz. The details of this theory are in process of elaboration by Professor J. J. Thomson.

Meantime, while the general opinion of physicists seems to be settling towards a wave or ether theory for the Röntgen rays, an opposite drift is apparent with respect to the physical nature of the cathode rays: it becomes more and more clear that cathode rays consist of electrified atoms or ions in rapid progressive motion. My idea of a fourth state of matter, propounded in 1881,* and at first opposed at home and abroad, is now becoming accepted. It is supported by Professor J. J. Thomson :† Dr. Larmor's theory‡ likewise involves the idea of an ionic substratum of matter; the view is also confirmed by Zeeman's phenomenon. In Germany, where the term cathode ray was invented almost as a protest against the theory of molecular streams propounded by me at the Sheffield meeting of the British Association in 1879, additional proofs have been produced in favour of the doctrine that the essential fact in the phenomenon is electrified Radiant Matter.

The speed of these molecular streams has been approximately measured, chiefly by aid of my own discovery nearly twenty years ago, that their path is curved in a magnetic field and that they produce phosphorescence where they impinge on an obstacle. The two unknown quantities, the charge and the speed of each atom, are measurable from the amount of curvature and by means of one other independent experiment.

It cannot be said that a complete and conclusive theory of these rays has yet been formulated. It is generally accepted that collisions among particles, especially the violent collisions due to their impact on a massive target placed in their path, give rise to the interesting kind of extremely high frequency radiation discovered by Röntgen. It has indeed for some time been known that whereas a charged body in motion constitutes an electric current, the sudden stoppage, or any violent acceleration of such a body, must cause an alternating electric disturbance, which though so rapidly decaying in intensity as to be practically "dead beat," yet must give rise to an ethereal wave or pulse travelling with the speed of light but of a length comparable to the size of the body whose sudden change of motion caused the disturbance. The emission of a high-pitched musical sound from the jolting of a dustman's cart (with a spring bell hung on it) has been suggested as an illustration of the way in which the molecules of any solid not at absolute zero may possibly emit such rays.

If the target on to which the electrically charged atoms impinge is so constituted that some of its minute parts can thereby be set into rhythmical vibration, the energy thus absorbed reappears in the form of light and the body is said to phosphoresce. The efficient action of the phosphorescent target appears to depend as much on its physical and molecular as on its chemical constitution. The best known phosphori belong to certain well-defined classes, such as the sulphides of the alkaline-earthy metals, and some of the so-called rare earths; but the phosphorescent properties of each of these groups are profoundly modified by an admixture of foreign bodies—witness the effect on the lines in the phosphorescent spectrum of yttrium and samarium produced by traces of calcium or lead. The persistence of the samarium spectrum in presence of overwhelming quantities of other metals is almost unexampled in spectroscopy: thus one part of samaria can easily be seen when mixed with three million parts of lime.

Without stating it as a general rule it seems as if with a non-phosphorescing target the energy of molecular impact reappears as pulses so abrupt and irregular that when resolved they furnish a copious supply of waves of excessively short wave-length, in fact the now well-known Röntgen rays. The phosphorescence so excited may last only a small fraction of a second, as with the constituents of yttria, where the duration of the different lines varies between the 0·003 and the 0·0009 second; or it may linger for hours, as in the case of some of the yttria earths, and especially with the earthy sulphides, where the glow lasts bright enough to be commercially useful. Excessively phosphorescent bodies can be excited by light waves, but most of them require the stimulus of electrical excitement.

It now appears that some bodies, even without special stimulation, are capable of giving out rays closely allied if not in some cases identical with those of Professor Röntgen. Uranium and thorium compounds are of this character, and it would almost seem from the important researches of Dr. Russell, that this ray-emitting power may be a general property of matter, for he has shown that nearly every substance is capable of affecting the photographic plate if exposed in darkness for sufficient time.

No other source for Röntgen rays but the Crookes tube has yet been discovered, but rays of kindred sorts are recognised. The Becquerel rays, emitted by uranium and its compounds, have now found their companions in rays—discovered almost simultaneously by Curie and Schmidt—emitted by thorium and its compounds. The thorium rays affect photographic plates through screens of paper or aluminium and are absorbed by metals and other dense bodies. They ionise the air, making it an electrical conductor; and they can be refracted and probably reflected, at least diffusively. Unlike uranium rays, they are not polarised by transmission through tourmaline, therefore resembling in this respect the Röntgen rays.

Quite recently M. and Mdme. Curie have announced a discovery which if confirmed cannot fail to assist the investigation of this obscure branch of physics. They have brought to notice a new constituent of the uranium mineral pitchblende, which in a 400-fold degree possesses Uranium's mysterious power of emitting a form of energy capable of impressing a photographic plate and of discharging electricity by rendering air a conductor. It also appears that the radiant activity of the new body, to which the discoverers have given the name of Polonium, needs neither the excitation of light nor the stimulus of electricity; like uranium, it draws its energy from some constantly regenerating and hitherto unsuspected store, exhaustless in amount.

It has long been to me a haunting problem how to reconcile this apparently boundless out-pour of energy with accepted canons. But as Dr. Johnstone Stoney reminds me, the resources of molecular movements are far from exhausted. There are many stores of energy in Nature that may be drawn on by properly constituted bodies without very obvious cause. Some time since I drew attention to the enormous amount of locked up energy in the ether; nearer our experimental grasp are the motions of atoms and molecules, and it is not difficult mentally so to modify Maxwell's demons as to reduce

* *Phil. Tranz.*, Part 2, 1881, pp. 433-4.
† *Phil. Mag.*, October, 1897, p. 312.
‡ *Phil. Mag.*, December, 1897, p. 506.

them to the level of an inflexible law and thus bring them within the ken of a philosopher in search of a new tool. It is possible to conceive a target capable of mechanically sifting from the molecules of the surrounding air the quick from the slow movers. This sifting of the swift moving molecules is effected in liquids whenever they evaporate, and in the case of the constituents of the atmosphere, wherever it contains constituents light enough to drift away molecule by molecule. In my mind's eye I see such a target as a piece of metal cooler than the surrounding air acquiring the energy that gradually raises its temperature from the outstanding effect of all its encounters with the molecules of the air about it; I see another target of such a structure that it throws off the slow moving molecules with little exchange of energy, but is so influenced by the quick moving missiles that it appropriates to itself some of their energy. Let uranium or polonium, bodies of densest atoms, have a structure that enables them to throw off the slow moving molecules of the atmosphere, while the quick moving molecules, smashing on to the surface, have their energy reduced and that of the target correspondingly increased. The energy thus gained seems to be employed partly in dissociating some of the molecules of the gas (or in inducing some other condition which has the effect of rendering the neighbouring air in some degree a conductor of electricity) and partly in originating an undulation through the ether, which, as it takes its rise in phenomena so disconnected as the impacts of the molecules of the air, must furnish a large contingent of light waves of short wave-length. The shortness in the case of these Becquerel rays appears to approach without attaining the extreme shortness of ordinary Röntgen rays. The reduction of the speed of the quick moving molecules would cool the layer of air to which they belong; but this cooling would rapidly be compensated by radiation and conduction from the surrounding atmosphere: under ordinary circumstances the difference of temperature would scarcely be perceptible and the uranium would thus appear to perpetually emit rays of energy with no apparent means of restoration.

The total energy of both the translational and internal motions of the molecules locked up in quiescent air at ordinary pressure and temperature is about 140,000 foot-pounds in each cubic yard of air. Accordingly the quiet air within a room 12 feet high, 18 feet wide, and 22 feet long, contains energy enough to propel a one-horse engine for more than twelve hours. The store drawn upon naturally by uranium and other heavy atoms only awaits the touch of the magic wand of Science to enable the Twentieth Century to cast into the shade the marvels of the Nineteenth.

Whilst placing before you the labours and achievements of my comrades in Science I seize this chance of telling you of engrossing work of my own on the fractionation of yttria, to which for the last eighteen years I have given ceaseless attention. In 1883, under the title of "Radiant Matter Spectroscopy," I described a new series of spectra produced by passing the phosphorescent glow of yttria, under molecular bombardment *in vacuo*, through a train of prisms. The visible spectra in time gave up their secrets, and were duly embalmed in the *Philosophical Transactions*. At the Birmingham Meeting of the British Association in 1886 I brought the subject before the Chemical Section, of which I had the honour to be President. The results led to many speculations on the probable origin of all the elementary bodies—speculations that for the moment I must waive in favour of experimental facts.

There still remained for spectroscopic examination a long tempting stretch of unknown ultra-violet light, of which the exploration gave me no rest. But I will not now enter into details of the quest of unknown lines. Large quartz prisms, lenses, and condensers, specially sensitised photographic films capable of dealing with the necessary small amount of radiation given by feebly phosphorescing substances,* and above all tireless patience in collating and interpreting results, have all played their part. Although the research is incomplete I am able to announce that among the groups of rare earths giving phosphorescent spectra in the visible region there are others giving well-defined groups of bands which can only be recorded photographically. I have detected and mapped no less than six such groups extending to λ 3060.

Without enlarging on difficulties, I will give a brief outline of the investigation. Starting with a large quantity of a group of the rare earths in a state of considerable purity, a particular method of fractionation is applied, splitting the earths into a series of fractions differing but slightly from each other. Each of these fractions, phosphorescing *in vacuo*, is arranged in the spectrograph, and a record of its spectrum photographed upon a specially prepared sensitive film.

In this way, with different groups of rare earths, the several invisible bands were recorded—some moderately strong, others exceedingly faint. Selecting a portion giving a definite set of bands, new methods of fractionation were applied, constantly photographing and measuring the spectrum of each fraction. Sometimes many weeks of hard experiment failed to produce any separation, and then a new method of splitting up was devised and applied. By unremitting work—the solvent of most difficulties—eventually it was possible to split up the series of bands into various groups. Then, taking a group which seemed to offer possibilities of reasonably quick result, one method after another of chemical attack was adopted, with the ultimate result of freeing the group from its accompanying fellows and increasing its intensity and detail.

As I have said, my researches are far from complete, but about one of the bodies I may speak definitely. High up in the ultra-violet, like a faint nebula in the distant heavens, a group of lines was detected, at first feeble and only remarkable on account of their isolation. On further purification these lines grew stronger. Their great refrangibility cut them off from other groups. Special processes were employed to isolate the earth, and using these lines as a test, and appealing at every step to the spectrograph, it was pleasant to see how each week the group stood out stronger and stronger, while the other lines of yttrium, samarium, ytterbium, &c., became fainter, and at last practically vanishing left the sought for group strong and solitary. Finally, within the last few weeks, hopefulness has merged into certainty, and I have absolute evidence that another member of the rare earth groups has been added to the list. Simultaneously with the chemical and spectrographic attack, atomic weight determinations were constantly performed.

As the group of lines which betrayed its existence stand alone, almost at the extreme end of the ultra-violet spectrum, I propose to name the newest of the elements Monium, from the Greek *μόνος*, alone. Although caught by the searching rays of the spectrum, Monium offers a direct contrast to the recently discovered gaseous elements, by having a strongly marked individuality; but although so young and wilful, it is willing to enter into any number of chemical alliances.

Until my material is in a greater state of purity I hesitate to commit myself to figures; but I may say that the wave-lengths of the principal lines are 3120 and 3117. Other fainter lines are at 3219, 3064, and 3060. The atomic weight of the element, based on the assumption of R_2O_3, is not far from 118,—greater than that accepted for yttrium and less than that for lanthanum.

I ought almost to apologise for adding to the already too long list of elements of the rare earth class,—the asteroids of the terrestrial family. But as the host of

* In this direction I am glad to acknowledge my indebtedess to Dr. Schumann, of Leipzig, for valuable suggestions and details of his own apparatus, by means of which he has produced some unique records of metallic and gaseous spectra of lines of short wave-length.

celestial asteroids, unimportant individually, become of high interest when once the idea is grasped that they may be incompletely coagulated remains of the original nebula, so do these elusive and insignificant rare elements rise to supreme importance when we regard them in the light of component parts of a dominant element, frozen in embryo, and arrested in the act of coalescing from the original protyle into one of the orderly and law abiding family for whom Newlands and Mendeleeff have prepared pigeon-holes. The new element has another claim to notice. Not only is it new in itself, but to discover it a new tool had to be forged for spectroscopic research.

Further details I will reserve for that tribunal before whom every aspirant for a place in the elemental hierarchy has to substantiate his claim.

These, then, are some of the subjects, weighty and far-reaching, on which my own attention has been chiefly concentrated. Upon one other interest I have not yet touched—to me the weightiest and the farthest reaching of all.

No incident in my scientific career is more widely known than the part I took many years ago in certain psychic researches. Thirty years have passed since I published an account of experiments tending to show that outside our scientific knowledge there exists a Force exercised by intelligence differing from the ordinary intelligence common to mortals. This fact in my life is of course well understood by those who honoured me with the invitation to become your President. Perhaps among my audience some may feel curious as to whether I shall speak out or be silent. I elect to speak, although briefly. To enter at length on a still debatable subject would be unduly to insist on a topic which,—as Wallace, Lodge, and Barrett have already shown,—though not unfitted for discussion at these meetings, does not yet enlist the interest of the majority of my scientific brethren. To ignore the subject would be an act of cowardice—an act of cowardice I feel no temptation to commit.

To stop short in any research that bids fair to widen the gates of knowledge, to recoil from fear of difficulty or adverse criticism, is to bring reproach on Science. There is nothing for the investigator to do but to go straight on, "to explore up and down, inch by inch, with the taper his reason;" to follow the light wherever it may lead, even should it at times resemble a will-o'-the wisp. I have nothing to retract. I adhere to my already published statements. Indeed, I might add much thereto. I regret only a certain crudity in those early expositions which, no doubt justly, militated against their acceptance by the scientific world. My own knowledge at that time scarcely extended beyond the fact that certain phenomena new to science had assuredly occurred, and were attested by my own sober senses, and better still, by automatic record. I was like some two-dimensional being who might stand at the singular point of a Riemann's surface, and thus find himself in infinitesimal and inexplicable contact with a plane of existence not his own.

I think I see a little farther now. I have glimpses of something like coherence among the strange elusive phenomena; of something like continuity between those unexplained forces and laws already known. This advance is largely due to the labours of another Association of which I have also this year the honour to be President—the Society for Psychical Research. And were I now introducing for the first time these inquiries to the world of science I should choose a starting-point different from that of old. It would be well to begin with *telepathy*; with the fundamental law, as I believe it to be, that thoughts and images may be transferred from one mind to another without the agency of the recognised organs of sense—that knowledge may enter the human mind without being communicated in any hitherto known or recognised ways.

Although the enquiry has elicited important facts with reference to the Mind, it has not yet reached the scientific stage of certainty which would entitle it to be usefully brought before one of our Sections. I will therefore confine myself to pointing out the direction in which scientific investigation can legitimately advance. If telepathy take place we have two physical facts—the physical change in the brain of A, the suggester, and the analogous physical change in the brain of B, the recipient of the suggestion. Between these two physical events there must exist a train of physical causes. Whenever the connecting sequence of intermediate causes begins to be revealed the enquiry will then come within the range of one of the Sections of the British Association. Such a sequence can only occur through an intervening medium. All the phenomena of the universe are presumably in some way continuous, and it is unscientific to call in the aid of mysterious agencies when with every fresh advance in knowledge it is shown that ether vibrations have powers and attributes abundantly equal to any demand—even to the transmission of thought. It is supposed by some physiologists that the essential cells of nerves do not actually touch, but are separated by a narrow gap which widens in sleep, while it narrows almost to extinction during mental activity. This condition is so singularly like that of a Branly or Lodge coherer as to suggest a further analogy. The structure of brain and nerve being similar, it is conceivable there may be present masses of such nerve coherers in the brain whose special function it may be to receive impulses brought from without through the connecting sequence of ether waves of appropriate order of magnitude. Röntgen has familarised us with an order of vibrations of extreme minuteness compared with the smallest waves with which we have hitherto been acquainted, and of dimensions comparable with the distances between the centres of the atoms of which the material universe is built up; and there is no reason to suppose that we have here reached the limit of frequency. It is known that the action of thought is accompanied by certain molecular movements in the brain, and here we have physical vibrations capable from their extreme minuteness of acting direct on individual molecules, while their rapidity approaches that of the internal and external movements of the atoms themselves.

Confirmation of telepathic phenomena is afforded by many converging experiments, and by many spontaneous occurrences only thus intelligible. The most varied proof, perhaps, is drawn from analysis of the sub-conscious workings of the mind, when these, whether by accident or design, are brought into conscious survey. Evidence of a region, below the threshold of consciousness, has been presented, since its first inception, in the *Proceedings of the Society for Psychical Research*; and its various aspects are being interpreted and welded into a comprehensive whole by the pertinacious genius of F. W. H. Myers. Concurrently, our knowledge of the facts in this obscure region has received valuable additions at the hands of labourers in other countries. To mention a few names out of many, the observations of Richet, Pierre Janet, and Binet (in France), of Breuer and Freud (in Austria), of William James (in America) have strikingly illustrated the extent to which patient experimentation can probe sub-liminal processes, and can thus learn the lessons of alternating personalities and abnormal states. Whilst it is clear that our knowledge of sub-conscious mentation is still to be developed we must beware of rashly assuming that all variations from the normal waking condition are necessarily morbid. The human race has reached no fixed or changeless ideal: in every direction there is evolution as well as disintegration. It would be hard to find instances of more rapid progress, moral and physical, than in certain important cases of cure by suggestion—again to cite a few names out of many—by Liébault, Bernheim, the late Auguste Voisin, Bérillon (in France), Schrenck-Notzing (in Germany), Forel (in Switzerland), van Eeden (in Holland), Wetterstrand (in Sweden), Milne-Bramwell and Lloyd Tuckey (in England). This is not the place for details, but the *vis*

medicatrix thus evoked, as it were, from the depths of the organism, is of good omen for the upward evolution of mankind.

A formidable range of phenomena must be scientifically sifted before we effectually grasp a faculty so strange, so bewildering, and for ages so inscrutable, as the direct action of mind on mind. This delicate task needs a rigorous employment of the method of exclusion—a constant setting aside of irrelevant phenomena that could be explained by known causes, including those far too familiar causes, conscious and unconscious fraud. The enquiry unites the difficulties inherent in all experimentation connected with *mind*, with tangled human temperaments and with observations dependent less on automatic record than on personal testimony. But difficulties are things to be overcome even in the elusory branch of research known as Experimental Psychology.

It has been characteristic of the leaders among the group of enquirers constituting the Society for Psychical Research to combine critical and negative work with work leading to positive discovery. To the penetration and scrupulous fairmindedness of Professor Henry Sidgwick and of the late Edmund Gurney is largely due the establishment of canons of evidence in psychical research, which strengthen while they narrow the path of subsequent explorers. To the detective genius of Dr. Richard Hodgson we owe a convincing demonstration of the narrow limits of human continuous observation.

It has been said that "Nothing worth the proving can be proved, nor yet dis-proved." True though this may have been in the past, it is true no longer. The Science of our century has forged weapons of observation and analysis by which the veriest tyro may profit. Science has trained and fashioned the average mind into habits of exactitude and disciplined perception, and in so doing has fortified itself for tasks higher, wider, and incomparably more wonderful than even the wisest among our ancestors imagined. Like the souls in Plato's myth that follow the chariot of Zeus, it has ascended to a point of vision far above the earth. It is, henceforth, open to Science to transcend all we now think we know of matter, and to gain new glimpses of a profounder scheme of Cosmic Law.

An eminent predecessor in this Chair declared that "by an intellectual necessity he crossed the boundary of experimental evidence, and discerned in that Matter, which we in our ignorance of its latent powers, and notwithstanding our professed reverence for its Creator, have hitherto covered with opprobrium, the potency and promise of all terrestrial life." I should prefer to reverse the apophthegm, and to say that in Life I see the promise and potency of all forms of Matter.

In old Egyptian days a well known inscription was carved over the portal of the temple of Isis:—"I am whatever hath been, is, or ever will be; and my veil no man hath yet lifted." Not thus do modern seekers after truth confront Nature—the word that stands for the baffling mysteries of the Universe. Steadily, unflinchingly, we strive to pierce the inmost heart of Nature, from what she is to re-construct what she has been, and to prophesy what she yet shall be. Veil after veil we have lifted, and her face grows more beautiful, august, and wonderful, with every barrier that is withdrawn.

(To be continued).

Allen's Commercial Organic Analysis. — We are glad to learn that the second edition of this well-known work is very near its completion. Its publishers, Messrs. J. and A. Churchill, announce the fourth (concluding) volume for issue in October. The first two volumes and the first part of the third have long been out of print, and second-hand copies have commanded a high price. The author, not being at present able to revise these as he would like, has willingly accepted the aid of Dr. Henry Leffmann, of Philadelphia, in making such addenda and editorial notes as are necessary to bring them in many important particulars up to date. Messrs. Churchill will publish Vol. I. almost immediately, and the other two will follow at no distant date.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 10th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month, one was found to be clear but dull, all the rest being clear, bright, and well filtered.

We have this month to record a very serious deficiency in the rainfall at Oxford. The actual amount which fell was but 0·53 inch. The average July fall for the past thirty years is 2·68 inches, leaving a deficiency of 2·15 inches. On the 1st July 0·22 inch of rain fell; rain also fell on five other days, but never so much as a tenth of an inch. The total deficiency for the year is now 5·49 inches.

Our bacteriological examinations of 258 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, standpipes, &c., making a total of 297 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	358
New River, filtered (mean of 26 samples) ..	12
Thames, unfiltered (mean of 26 samples)	1132
Thames water, from the clear water wells of five Thames-derived supplies (mean of 128 samples)	40
Ditto ditto .. .. highest	682
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	3080
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	35

The quality of the water supplied to the Metropolis during the month of July has been very similar to that of last month, and is of excellent character both in colour and in freedom from organic impurity.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmiting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Gasoline.—A correspondent wishes to know how gasoline is manufactured.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2025.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Bristol, 1898.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir William Crookes, F.R.S., V.P.C.S.

(Concluded from p. 135).

APPENDIX.

In preparing the part of this address dealing with the world's supply and demand for wheat, and the conclusions based thereon, I have been materially assisted by Mr. C. Wood Davis, of Kansas, U.S.A. Apart from information obtained from Mr. Davis's articles in *The Forum*, the *North-Western Miller*, the *New York Sun*, and other papers, I am indebted to him for valuable manuscript information on matters of detail. Mr. Davis appears to be the only person dealing with this problem in a manner to determine such essential factors as average acre yields for long periods, unit requirements for each of the primary food staples of the temperate zones, and the ratios existing during different recent periods between the consuming element and acres employed in the production of each of such primary food staples. His scientific method enables him to ascertain the acreage requirements of the separate national populations, and of the "bread-eating" world as a whole. Information has also been obtained from the "Agricultural Returns of the United Kingdom," the official "Reports on Agricultural Depression," and the Annual Reports of the United States Secretary of Agriculture; likewise from papers and articles by Sir John Lawes, Sir H. Gilbert, Major Craigie, Mr. W. E. Bear, Mr. Warington, Professor E. M. Shelton, Mr. R. F. Crawford, Dr. Newton, and Mr. W. Walgrave Chapman. The *Journal of the Royal Agricultural Society*, the *Journal of the Royal Statistical Society*, the *Journal of the Board of Agriculture*, and other periodicals have also been laid under contribution. I am also indebted to the various official publications of the Government of Canada, the Department of Agriculture, Queensland, and to friends all over the world.

A.

Last year there were under corn crops in the United Kingdom:—

Wheat ..	3025 sq. miles,	producing 56,296,000 bushels.
Barley ..	3447 "	
Oats ..	6580 "	
Total ..	13,052 "	

There is now about as much area under mixed cereals as would have to be devoted solely to wheat to make our country self-supporting.

B.

The World's Wheat Crop of 1897-98 *from Contributory Areas.*

	Bushels.
United States	510,000,000
France	240,000,000
Russia and Poland	230,000,000
Austria-Hungary	135,000,000
Germany	105,000,000
Spain	96,000,000
Italy	82,000,000
Trans-Caucasia and Siberia	64,000,000
Argentina	60,000,000
United Kingdom	56,000,000
Canada	55,000,000
Rumania	43,000,000
Caucasia (Northern)	40,000,000
Australasia	38,000,000
Bulgaria	30,000,000
Turkey in Europe	22,000,000
Belgium	16,000,000
Chili	15,000,000
Uruguay, Brazil, &c.	9,000,000
Portugal	7,000,000
Servia	6,000,000
Holland	5,000,000
Denmark	5,000,000
Sweden and Norway	5,000,000
Greece	4,000,000
Switzerland	4,000,000
Bosnia, Montenegro, Cyprus, &c.	4,000,000
South Africa	4,000,000
	1,890,000,000
Add imports from Asia and North Africa	31,000,000
Total available wheat supply	1,921,000,000*

Table showing the Variations in the Bread-eating Populations and the Available Supply of Wheat in the Five-Yearly Periods from 1878 *to* 1897, *in Millions of Bushels, and Annual Averages.*

Years.	Bread-eating populations.	Wheat grown by "contributory areas."	Imports from Asia and North Africa.	Remainders from former harvest.	Total available supply.	Required for seed and food.	Supply in excess of year's needs.
1877-81	407·0	1797·0	13·8	174·4	1985·2	1812·8	172·4
1882-86	432·8	1937·6	41·4	294·0	2273·0	1946·0	327·0
1887-91	460·8	2043·5	43·2	260·2	2346·9	2102·0	244·9
8192-96	490·9	2199·2	23·6	265·4	2488·2	2233·8	254·4
1897-98	510·0	1890·0	31·0	300·0	2221·0	2310·0	Deficit 89·0

C.

The "world's demand" for wheat is as follows:—

	Bushels.
United Kingdom, about	180,000,000
Belgium	24,000,000
Germany	35,000,000
Holland	13,000,000
Switzerland	13,500,000
France	40,000,000
Sweden	4,000,000
Spain	10,000,000
Portugal	4,000,000
Greece	4,500,000
Islands and tropical lands	28,000,000
Total	356,000,000

D.

Between 1882 and 1897 the wheat crops were so abundant that over 1200 million bushels were added to our stores, besides large accumulations of rye. During this time of golden harvests, the exports from Russia increased, in consequence of the Russian decline in unit

* Outside the better known areas of wheat supply a certain proportion of wheat comes from India, Persia, Syria, Anatolia, and North Africa. But it is impossible to get accurate figures as to acreage and yield from these countries; as bread-eaters derive less than 1 per cent of their supplies from these outlying sources, it is convenient to call the ordinary areas "contributory areas," and to deal with the external areas no further than to show the volume of imports yielded from year to year.

consumption of 13·5 per cent. These reserves have been gradually drawn upon, but enough still remained to obscure the fact that the 1895-6 harvest was 75,000,000 bushels, and the 1896-7 harvest was 138,000,000 bushels below current needs.

The following table* has been compiled from statistics carefully collected by Mr. Davis and other observers. The prophetic figures are on the assumption that population, unit consumption, and steady development will increase during the next forty-three years as they have increased since 1871:—

Date.	Bread-eaters.	Food and seed† required per unit. Bushels.	Requiring bushels of wheat.	With yields averaging 12·7 bushels, acreage required.
1871	371,000,000	4·15	1,540,000,000	121,000,000
1881	416,000,000	4·38	1,822,000,000	143,000,000
1891	472,600,000	4·50	2,127,000,000	167,000,000
1898	516,500,000	4·50	2,324,000,000	183,000,000
1901	536,100,000	4·50	2,412,000,000	190,000,000
1911	603,700,000	4·50	2,717,000,000	214,000,000
1921	674,000,000	4·50	3,033,000,000	239,000,000
1931	746,100,000	4·50	3,357,000,000	264,000,000
1941	819,200,000	4·50	3,686,000,000	290,000,000

To supply these bread-eaters, the world inhabited by bread-eating populations grew the following quantities of wheat in each of the designated five-year periods:—

Years.	Bushels. Annual average.	Acres. Annual average.
1871-75	1,580,000,000, grown on	131,000,000
1876-80	1,746,000,000 ,,	143,000,000
1881-85	1,926,000,000 ,,	152,000,000
1886-90	1,987,000,000 ,,	154,000,000
1891-95	2,201,000,000 ,,	159,000,000

Within the same periods wheat was imported from Asia and North Africa by the "bread-eating" countries as follows:—

Years.	Bushels. Annual average.	Acres. Annual average.
1871-75	8,000,000, the net product of	750,000
1876-80	12,000,000 ,, ,,	1,120,000
1881-85	36,000,000 ,, ,,	3,360,000
1886-90	39,000,000 ,, ,,	3,640,000
1891-95	34,000,000 ,, ,,	3,200,000

Broadly speaking, 2000 million bushels are now consumed in the countries where they are grown, either as food or for seed, while the balance is exported.

E.

At the present time the disproportion is even higher, owing to unit consumption gradually increasing from year to year accompanied by slow shrinkage in the wheat area.

	1871.	1884.	1897.	Per cent of increase or decrease in twenty-six years.
Population..	371,000,000	432,800,000	510,000,000	37·5 increase.
Wheat acres	125,800,000	154,300,000	158,000,000	25·6 increase.
Rye acres ..	111,000,000	110,300,000	106,500,000	4·1 decrease.

* I have taken the unit consumption including seed at 4·5 bushels and the yield per acre at 12·7 bushels per annum, this being the average of the whole world. The exact yield varies with the country in which wheat is grown, as shown by the following table:—

Average Yield of Wheat per Acre in—

	Bushels.		Bushels.
Denmark	41·8	Poland	16·2
United Kingdom	29·1	Canada	15·5
New Zealand	25·5	Argentina	13·0
Norway	25·1	Italy	12·1
Germany	23·2	United States (mean) .	12·0
Belgium	21·5	India	9·2
Holland	21·5	Russia in Europe ..	8·6
France	19·4	Algeria	7·5
Hungary	18·6	South Australia	7·0
Rumania	18·5	Australasia	6·8
Austria	16·3		

† The seed quota is kept constant at 0·6 bushel per unit per annum, but the unit food requirements are found to increase in each five-yearly period. There has been a steady increase of unit wheat requirements by reason of the decrease of unit consumption of rye, maslin, spelt, and buckwheat.

The area planted with the two great bread-making grains is actually less now than thirteen years ago, despite enormous additions to the population. The area under *all* the bread-making grains is absolutely 2·2 per cent less than thirteen years ago, notwithstanding an increase of one-fifth in requirements for bread.

F.

Notwithstanding this expansion the supplies of wheat were hardly sufficient for the food demands of the world. As the area under wheat has increased that under rye has diminished, with the result that scarcely an acre has been added to the world's wheat and rye since 1890; and there was in 1897 a deficit in the two principal bread-making grains of more than 600,000,000 bushels.

G.

Stocks of wheat and flour in the United States were, relatively to population, probably never smaller, if so small as now. The following table (from *Bradstreet*) shows the visible supply of wheat in the States on June 1 since 1893:—

	Bushels.		Bushels.
1893	93,700,000	1896	71,300,000
1894	80,500,000	1897	39,200,000
1895	72,800,000	1898	32,500,000

H.

In 1896 the area under wheat in the Governments of Russia and Poland was 36,000,000 acres. But the yearly consumption of wheat per head during the last ten years has declined 14 per cent, and the consumption of bread is quite 30 per cent less than is required to keep the population in health. The grain reserved for seed has likewise decreased—the peasantry limiting their sowing with the rise of taxation. The reduction of 14 per cent in the unit consumption of bread in Russia has added, during the last eighteen years, 1,360,000,000 bushels to the general wheat supply. This factitious excess temporarily staved off scarcity in Europe.

I.

In the year 1897 there were 2,371,441 acres under cultivation in Manitoba, out of a total of 13,051,375 acres. The total area includes water courses, lakes, forests, towns, and farms, land unsuitable for wheat growing, and land required for other crops.

J.

The most trustworthy estimates give Canada a wheat area of not more than six millions of acres in the next twelve years, increasing to a maximum of twelve millions of acres in twenty-five years. The development of this promising area necessarily must be slow, since prairie land cannot be laid under wheat in advance of a population sufficient to supply the needful labour at seed time and harvest. As population increases so do home demands for wheat.

Acreage, Crop, and Exports of Wheat from Canada from 1891 to 1897.

Year.	Population.	Acres.	Total bushels.	Bushels exported.
1891	4,833,000	2,690,000	62,600,000	3,000,000
1892	4,885,000	2,910,000	49,700,000	10,200,000
1893	4,936,000	2,800,000	42,700,000	11,000,000
1894	4,986,000	2,550,000	44,600,000	11,000,000
1895	5,040,000	2,560,000	57,500,000	9,200,000
1896	5,090,000	2,700,000	40,800,000	10,400,000
1897	5,140,000	2,900,000	56,600,000	8,000,000

The net exports average 8,970,000 bushels yearly, being 24·3 per cent of the net product.

K.

The land under wheat in Austro-Hungary, according to the latest official figures, is eleven million acres. The 1897-8 crop, including that of Croatia-Slavonia, is fifty-five million bushels below that of 1896-7, and as exports

during the last five years have averaged less than 4,000,000 bushels per annum, the imports of wheat are expected to be large.

L.

So long ago as April 16, 1891, the following statement by a leading Indian economist appeared in the *Daily Englishman* of Calcutta:—"People do not realise the fact that all the wheat India produces is required for home consumption, and that this fact is not likely to be realised until a serious disaster occurs, and that even now less than 9 per cent is exported. It is a self-evident fact that a slight expansion of consumption, or a partial failure of crops of other food grains, will be sufficient to absorb the small proportion now exported. Besides, we have a steady increase of consumption, in consequence of the natural growth of the population, as well as in the gradual improvement of the condition of a considerable part of the people in the cities. I believe that, comparatively speaking, India will in a few years cease to export wheat, and soon thereafter become an importing country."

M.

An average wheat crop on the 1897-8 acreage would be 2,070,000,000 bushels. Adding to this 1,270,000,000 bushels, makes a grand total of 3,340,000,000 bushels. But the estimate in Appendix D shows that in the year 1931 the bread eaters will require 3,357,000,000 bushels. Thus there will be in 1931 a deficiency of 17,000,000 bushels, unless the average yield per acre be increased.

N.

Sir Andrew Noble informs me that a first-class battleship would carry about sixty-three tons of cordite, and we may suppose that in a general action forty tons of this would be expended. Now at Trafalgar, Nelson had twenty-seven line-of-battle ships, and the allied forces thirty-three. If we suppose a similar number of modern battleships and first-class cruisers to be engaged, and each to expend forty tons of cordite, the total volume of nitrogen set free would be 302,400 cubic metres, or about 380 tons, equivalent to 2300 tons of nitrate of soda.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

BRISTOL, 1898.

By Professor F. R. JAPP, M.A., LL.D., F.R.S., President of the Section.

Stereochemistry and Vitalism.

Of the numerous weighty discoveries which science owes to the genius of Pasteur, none appeals more strongly to chemists than that with which he opened his career as an investigator—the establishing of the connection between optical activity and molecular symmetry in organic compounds. The extraordinary subtlety of the modes of isomerism then for the first time disclosed; the novelty and refinement of the means employed in the separation of the isomerides; the felicitous geometrical hypothesis adopted to account for the facts—an hypothesis which subsequent investigation has served but to confirm; the perfect balance of inductive and deductive method; and lastly, the circumstance that in these researches Pasteur laid the foundation of the science of stereochemistry: these are characteristics any one of which would have sufficed to render the work eminently noteworthy, but which, taken together, stamp it as the capital achievement of organic chemistry.

Physiologists, on the other hand, are naturally more attracted by Pasteur's subsequent work, in which the biological element predominates; in fact, I doubt whether many of them have given much attention to the earlier work. And yet it ought to be of interest to physiologists, not merely because it is the root from which the later work springs, but because it furnishes, I am convinced, a reply to the most fundamental question that physiology can propose to itself—namely, whether the phenomena of life are wholly explicable in terms of chemistry and physics; in other words, whether they are reducible to problems of the kinetics of atoms, or whether, on the contrary, there are certain residual phenomena, inexplicable by such means, pointing to the existence of a directive force which enters upon the scene with life itself, and which, whilst in no way violating the laws of the kinetics of atoms—whilst, indeed, acting through these laws—determines the course of their operation within the living organism.

The latter view is known as Vitalism. At one time universally held, although in a cruder form than that just stated, it fell, later on, into disrepute; "vital force," the hypothetical and undefined cause of the special phenomena of life, was relegated to the category of occult qualities; and the problems of physiology were declared to be solely problems of chemistry and physics. Various causes contributed to this result. In the first place, the mere name "vital force" explains nothing; although, of course, one may make this admission without thereby conceding that chemistry and physics explain everything. Secondly, the older vitalists confounded force with energy; their "vital force" was a source of energy; so that their doctrines contradicted the law of the conservation of energy, and became untenable the moment that this law was established. I would point out, however, that the assumption of a purely directive "vital force," such as I have just referred to, using the word "force" in the sense which it bears in modern dynamics, does not *necessarily* involve this contradiction; for a force acting on a moving body at right angles to its path does no work, although it may continuously alter the direction in which the body moves. When, therefore, Professor J. Burdon Sanderson writes—"The proof of the non-existence of a special 'vital force' lies in the demonstration of the adequacy of the known sources of energy in the organism to account for the actual day by day expenditure of heat and work," he does not consider this special case. The application of the foregoing principle of dynamics to the discussion of problems like the present is, I believe, due to the late Professor Fleeming Jenkin. A third ground for abandoning the doctrine of a "vital force" was the discovery that numerous organic compounds for the production of which the living organism was supposed to be necessary, could be synthesised by laboratory methods from inorganic materials. It is the validity of some of the conclusions drawn from the latter fact that I wish especially to consider.

Recent years, have, however, witnessed a significant revival of the doctrine of vitalism among the physiologists of the younger generation.

It is not my intention to offer any opinion on the various arguments which physiologists of the neo-vitalistic school have put forward in support of their views; these arguments and the facts on which they are based lie entirely outside my province. I shall confine myself to a single class of chemical facts rendered accessible by Pasteur's researches on optically active compounds, and, considering these facts in the light of our present views regarding the constitution of organic compounds, I shall endeavour to show that living matter is constantly performing a certain geometrical feat which dead matter, unless indeed it happens to belong to a particular class of products of the living organism and to be thus ultimately referable to living matter, is incapable—not even conceivably capable—of performing. My argument, being based on geometrical and dynamical considerations, will have the advantage, over the physiological arguments, of immeasurably greater simplicity; so that, at all events, any fallacy into which I may unwittingly fall will be the more readily detected.

In order to make clear the bearing of the results of

stereochemical research on this physiological problem, it will be necessary to give a brief sketch of the stereochemistry of optically active organic compounds, as founded by Pasteur and as further developed by later investigators.

Substances are said to be optically active when they produce rotation of the plane of polarisation of a ray of polarised light which passes through them. The rotation may be either to the right or to the left, according to the nature of the substance; in the former case the substance is said to be dextro-rotatory; in the latter, lævo-rotatory. The effect is as if the ray had been forced through a twisted medium—a medium with a right-handed or a left-handed twist—and had itself received a twist in the process; and the amount of the rotation will depend upon the degree of "twist" in the medium (that is, on the rotatory power of substance) and upon the thickness of the stratum of substance through which the ray passes, just as the angle through which a bullet turns in passing from the breech to the muzzle of a rifle will depend upon the degree of twist in the rifling and the length of the barrel. If the bullet had passed through the barrel in the opposite direction, the rotation would still have been in the same sense; since a right-handed (or left-handed) twist or helix remains the same from whichever end it is viewed, in whichever direction it is traversed. This also applies to optically active substances; if the polarised ray passes through the substance in the opposite direction, the rotation still occurs in the same sense as before. This characteristic sharply distinguishes the rotation due to optically active substances from that produced by the magnetic field, the latter rotation being reversed on reversing the direction of the polarised ray.

Optically active substances may be divided into two classes. Some, like quartz, sodium chlorate, and benzil, produce rotation only when in the crystallised state; the dissolved (or fused) substances are inactive. Others, like oil of turpentine, camphor, and sugar, are optically active when in the liquid state or in solution. In the former case the molecules of the substance have no twisted structure, but they unite to form crystals having such a structure. As Pasteur expressed it, we may build up a spiral staircase—an asymmetric figure—from symmetric bricks; when the staircase is again resolved into its component bricks, the asymmetry disappears. (I will explain presently the precise significance of the terms symmetry and asymmetry as used in this connection). In the case of compounds which are optically active in the liquid state, the twisted structure must be predicated of the molecules themselves; that is, there must be a twisted arrangement of the atoms which form these molecules.

The earliest known experimental facts regarding the rotation of the plane of polarisation by various substances, solid and liquid, were discovered by Arago and by Biot.

After this preliminary statement as to what is understood by optical activity, we may consider Pasteur's special contributions to the solution of the problems involved.

Pasteur tells us, in the well-known "Lectures on the Molecular Asymmetry of Natural Organic Products," which he delivered in 1860, before the Chemical Society of Paris, that his earliest independent scientific work dealt with the subject of crystallography, to which he had turned his attention from a conviction that it would prove useful to him in the study of chemistry. In order to perfect himself in crystallographical methods, he resolved to repeat all the measurements contained in a memoir by De la Provostaye on the crystalline forms of tartaric acid, racemic acid, and their salts. These two sets of compounds have the same composition, except that they frequently differ in the number of molecules of water of crystallisation which they contain; but whereas tartaric acid and the tartrates are dextro-rotatory, racemic acid and the racemates are optically inactive. It was probably this circumstance that decided Pasteur in his choice of a subject, for it appears that, even as a student, he had been attracted by the problem of optical activity. In the course of the repetition, however, he detected a fact which had escaped the notice of his predecessor in the work, accurate observer as the latter was—namely, the presence, in the tartrates, of right-handed hemihedral faces, which are absent in the racemates. Hemihedral faces are such as occur in only half their possible number; and in the case of non-superposable hemihedry, to which class that of the tartrates belongs, there are always two opposite hemihedral forms possible—a right-handed or dexto- form, and a left handed or lævo- form. Which is right, and which is left, is a matter of convention; but they are opposite forms, and differ from one another exactly as the right hand of the human body differs from the left: that is, they resemble one another in every respect, except that they are non-superposable—the one cannot be made to coincide in space with the other, just as a right hand will not fit into a left-hand glove. The one form is identical with the mirror image of the other: thus the mirror image of a right hand is a left hand. Such opposite hemihedral crystalline forms are termed *enantiomorphs;* they have the same faces and the same angles, but differ in the fact that all positions in the one are reversed in the other for one dimension of space, and left unchanged for the other two dimensions; this being the geometrical transformation which an object appears to undergo when reflected in a plane mirror. Enantiomorphism is possible only in the case of asymmetric solid figures: these alone give non-superposable mirror images. Any object which gives a mirror image identical with the object itself—a superposable mirror image—must have at least one plane of symmetry.

The hemihedry of the tartrates discovered by Pasteur is in every case in the same sense—that termed right-handed—provided that the crystals are oriented according to two of the axes which have nearly the same ratio in all the tartrates.

Pasteur was inclined to connect the molecular dextro-rotatory power of the tartrates with this right-handed hemihedry; since in the racemates both the hemihedry and the rotatory power were absent. A similar connection, which, however, held good only for the crystalline condition, had, as he points out, been already observed in the case of quartz, the crystals of which occasionally exhibit small asymmetric (tetartohedral) faces, situated in some specimens to the right and in others to the left; the former specimens being dextro-, the latter lævo-rotatory. The possibility of this connection was first suggested by Sir John Herschel.

Pasteur's views were confirmed by an unexpected discovery which he made shortly after. Mitscherlich had stated, in 1844, in a communication to Biot, which the latter laid before the French Academy of Sciences, that sodium ammonium tartrate and sodium ammonium racemate were identical, not merely in chemical composition, but in crystalline form, in specific gravity, and in every other property, chemical and physical, except that the solution of the former salt was dextro-rotatory, that of the latter inactive. And to make his statement still more definite, he added:—"The nature and the number of the atoms, their arrangement, and their distances from one another, are the same in both compounds."

At the time this passage appeared, Pasteur was a student in the Ecole Normale. He tells us how it puzzled him, as being in contradiction to the views universally held by physicists and chemists that the properties, chemical and physical, of substances depended on the nature, number, and arrangement of their constituent atoms. He now returned to the subject, imagining that the explanation would be found in the fact that Mitscherlich had overlooked the hemihedral faces in the tartrate, and that the racemate would not be hemihedral. He therefore prepared and examined the two double salts. He found that the tartrate was, like all the other tartrates which he had investigated, hemihedral; but, to his surprise, the solution of the racemate also deposited

hemihedral crystals. A closer examination, however, disclosed the fact that, whereas in the tartrate all the hemihedral faces were situated to the right, in the crystals from the solution of the racemate they were situated sometimes to the right and sometimes to the left. Mindful of his view, regarding the connection between the sense of the hemihedry and that of the optical activity, he carefuly picked out and separated the dextro- and lævo-hemihedral crystals, made a solution of each kind separately, and observed it in the polarimeter. To his surprise and delight, the solution of the right-handed crystals was dextro-rotatory; that of the left-handed, lævo-rotatory. The right-handed crystals were identical with those of the ordinary (dextro-) tartrate; the others, which were their mirror image, or enantiomorph, were derived from the hitherto unknown lævo-tartaric acid. From the dextro- and lævo-salts, thus separated, he prepared the free dextro- and lævo-tartaric acids. And having thus obtained from racemic acid its two component acids—dextro- and lævo-tartaric acids—it was an easy matter to re-compose racemic acid. He found that, on mixing equal weights of the two opposite acids, each previously dissolved in a little water, the solution almost solidified, depositing a mass of crystals of racemic acid.

These two tartaric acids have the same properties, chemical and physical, except where their opposite asymmetry comes into play. They crystallise in the same forms, with the same faces and angles; but the hemihedral facets, which in the one are situated to the right, are, in the other, situated to the left. Their specific gravities and solubilities are the same; but the solution of the one is dextro-rotatory; of the other, lævo-rotatory. The salts which they form with inorganic bases also agree in every respect, except as regards their opposite asymmetry and opposite rotatory power. They are enantiomorphous.

Pasteur, discussing the question of the molecular constitution of these acids, anticipates in a remarkable manner the views at present held by chemists. "We know, on the one hand," he says, "that the molecular structures of the two tartaric acids are asymmetric, and on the other, that they are rigorously the same, with the sole difference of showing asymmetry in opposite senses. Are the atoms of the right acid grouped on the spirals of a right-handed helix, or placed at the solid angles of an irregular tetrahedron, or disposed according to some particular asymmetric grouping or other? We cannot answer these questions. But it cannot be a subject of doubt that there exists an arrangement of the atoms in an asymmetric order having a non-superposable image. It is not less certain that the atoms of the left acid realise precisely the asymmetric grouping which is the inverse of this."

The idea of the irregular tetrahedron is, it may be explained, derived from the hemihedral facets. Imagine these to develop in the case of dextro-tartaric acid until the other faces of the crystal disappear, and there results an irregular tetrahedron. Repeat the process with a crystal of lævo-tartaric acid, and the enantiomorphous tetrahedron—the mirror-image of the former—is obtained. We shall see later that the idea, on the one hand, of two asymmetric tetrahedra, and, on the other, that of two opposite helices, given as alternatives by Pasteur to explain the grouping of the atoms within the molecules of dextro- and lævo-tartaric acids, are in reality identical.

The precision of Pasteur's views as to the asymmetry of these acids enabled him to discover two further methods of separating them. Thus he points out that although these acids will possess equal affinity for any given symmetric base, such as potash, or ammonia, or aniline, yet their affinities will not be equal if the base, like quinine or strychnine, is itself asymmetric; because here the special one-sided asymmetry of the base will modify its mode of combination with the two enantiomorphous acids. The solubility is different in the case of the dextro- and lævo-tartrates of the same asymmetric base; the crystalline form, the specific gravity, the number of molecules of water of crystallisation, may be all different. Potassium dextro- and lævo-tartrates are mirror-images of one another; quinine dextro- and lævo-tartrates are not. Pasteur employed in his experiments the asymmetric base cinchonicine, which he converted into its acid racemate, and allowed the solution to crystallise. The first crystallisations consisted of pure lævo-tartrate of cinchonicine, whilst the more soluble dextro-tartrate remained in the mother-liquor, from which it finally crystallised in forms totally distinct from those of the lævo-tartrate.

Pasteur's third method is of physiological interest, and is, moreover, the stepping-stone to his later work on ferments. As we shall see presently, he regarded the formation of asymmetric organic compounds as the special prerogative of the living organism. Most of the substances of which the animal and vegetable tissues are built up—the proteids, cellulose—are asymmetric organic compounds, displaying optical activity. Pasteur had shown that two compounds of inverse asymmetry behaved differently towards a third asymmetric compound How would they behave towards the asymmetric living organism?

It had frequently been noticed that impure calcium tartrate, when mixed with organic matters, as is the case when it is obtained in the process of preparing tartaric acid from argol, readily underwent fermentation. Pasteur examined the action of the ferment (apparently a *Penicillium*) on ammonium tartrate—a substance which had the advantage over calcium tartrate of being soluble—and finding that the fermentation here followed a normal course, ending with the destruction of the tartrate, repeated the experiment with ammonium racemate, examining the solution from time to time with the polarimeter. The fermentation proceeded, apparently, as before; but the solution, originally optically inactive, became lævo-rotatory, the activity gradually increasing in amount until a maximum was reached. At this point the fermentation ceased. The whole of the dextro-tartrate had disappeared, and from the solution the lævo-tartrate was obtained in a state of purity. The asymmetric living organism had selected for its nutriment that particular asymmetric form of tartaric acid which suited its needs—the form, doubtless, which in some way fitted its own asymmetry—and had left the opposite form either wholly or, for the most part, untouched. The asymmetric micro-organism, therefore, exhibits a power which no symmetric chemical substance, such as our ordinary oxidising agents, and no symmetric form of energy, such as heat, can ever possess: it distinguishes between enantiomorphs. If we oxidise racemic acid with nitric acid, for example, both the enantiomorphous constituents are attacked in exactly the same degree. If we heat racemic acid, whatever happens to its right-handed constituent happens equally to its left-handed constituent: the temperature of decomposition of both is the same. Asymmetric agents can alone display selective action in dealing with enantiomorphs.

By the action of heat Pasteur converted ordinary tartaric acid into racemic acid, in which process a portion of the right acid is converted into the left, an equilibrium being established; and lævo-tartaric acid may be converted into racemic acid in the same way, the inverse change taking place. At the same time, a new tartaric acid is formed in both cases: mesotartaric acid, or true inactive tartaric acid, which resembles racemic acid in having no action on the plane of polarisation, but differs from it in not being separable into two acids of opposite activity. According to our present views, it contains two equal and opposite asymmetric groups *within* its molecule. Racemic acid is thus inactive by *inter*molecular compensation; mesotartaric acid by *intra*molecular compensation.

Pasteur, generalising somewhat hastily from the few cases which he had studied, came to the conclusion that

all organic compounds capable of exhibiting optical activity might exist in the foregoing four forms—dextro, lævo, racemoid, and meso. As regards the dextro and lævo forms, this is correct; as regards the racemoid form it is generally correct; but the meso form, as we now know, is a very special case, implying that the molecule contains two structurally identical complexes of opposite asymmetry.

Were I following the exact historical order, I should introduce here Pasteur's view that compounds exhibiting optical activity have never been obtained without the intervention of life—a view which it is the object of the present address to consider. The later developments of stereochemistry, however, throw so much light on this question, and enable us to discuss it with such precision, that we shall turn our attention to these first. Before so doing, however, we may note that, in spite of the immense growth in the material of stereochemistry, and in spite of the development of the theoretical views of stereochemists, hardly any experimental method of fundamental importance for the separation and transformation of optically active compounds has been added to those described in Pasteur's classical researches, although it is almost forty years since these came to a close. Perhaps Walden's remarkable discovery of a method for the transformation of certain enantiomorphs into their optical opposites without previous racemisation, is the only one entitled to be so classed.

Pasteur was in advance of his time, and his theory of molecular asymmetry was a seed that lay for many years in the ground without germinating.

In 1858, just about the period when Pasteur was concluding his researches in the foregoing field, Kekulé published his celebrated theoretical paper, "On the Constitution and Metamorphoses of Chemical Compounds, and on the Chemical Nature of Carbon," in which he showed that, by assuming that the carbon atom had four units of affinity, the constitution of organic compounds could be satisfactorily explained. This was the starting-point of the theory of chemical structure, and from that time to the present day organic chemists have been engaged, with enormous expenditure of labour, in determining the constitution or molecular structure of the carbon compounds on the lines of Kekulé's theory.

In order that Pasteur's ideas should bear fruit it was only necessary that his purely general statements with regard to molecular asymmetry should be specialised, so as to include the recognised constitution of organic compounds. It was from this union of Pasteur's theory with that of Kekulé that modern stereochemistry sprang. The necessary step was taken, independently and almost simultaneously, by van't Hoff and Le Bel, in 1874. I will briefly state their conclusions, so far as these bear on the subject of optical activity.

If we examine the structural formulæ of a number of thoroughly investigated optically active organic compounds, we shall find that the molecule of each contains at least one carbon atom of which the four affinities are satisfied by four different atoms or groups—an asymmetric carbon atom, as it is termed.

The four affinities, or directed attractive powers, of the carbon atom are not to be conceived of as lying in one plane. The simplest assumption that we can make with regard to their distribution in space is that the direction of each makes equal angles with the directions of the three others. We may express this differently by saying that the four atoms or groups attached to the carbon atom are situated at the solid angles of a tetrahedron, in the centre of which the carbon atom itself is placed. If the four atoms or groups are all identical they will be equally attracted by the carbon atom; consequently they will be equidistant from it, and the tetrahedron will be regular. If they are all different the force with which each is attracted will be different; they will arrange themselves at different distances from the carbon atom; and the tetrahedron will he irregular; it will have no plane of symmetry. Any compound of the formula CHX'Y'Z' can therefore exist in two enantiomorphs, applying this term to the molecules themselves—in two non-superposable forms, each of which is the mirror image of the other: thus—

Fig. 1.

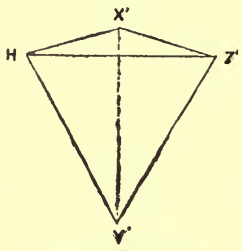
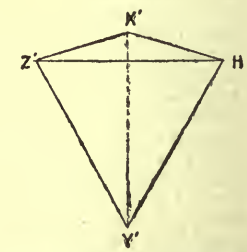


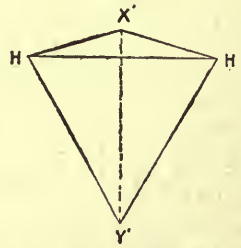
Fig. 2.



(In these figures no attempt has been made to represent the tetrahedra as irregular; the opposite asymmetry is indicated merely by the opposite order of the four attached atoms or groups. In reality, however, they would be irregular. The carbon atom itself is not shown).

If we consider any particular set of three atoms or groups—for example, H, Z', and Y'—looking towards that face of the tetrahedron about which they are arranged, any order, thus HZ'Y', which is clockwise in one figure, will be counter-clockwise in the other. In like manner, a continuous curve, passing through the four atoms or groups in any given sequence, will form a right-handed helix in the one case and a left-handed helix in the other. We thus find that the foregoing assumptions—the very simplest that could be made—regarding the distribution of the four affinities of carbon and the different degree with which four different atoms or groups will be attracted by the carbon atom to which they are attached, lead to the asymmetric structures postulated by Pasteur to account for optical activity—namely, enantiomorphous irregular tetrahedra, and right- and left-handed helices.

Fig. 3.



That a spiral arrangement, right- or left-handed, will produce rotation of the plane of polarisation in its own sense, may be shown by various experiments: thus in Reusch's optically active piles of plates of mica, produced by crossing successive plates of biaxal mica at an angle of 60° to one another; or in the twisted jute fibres recently described by Professor Bose, which, according to the direction of the twist previously imparted to them, rotate the plane of polarisation of electric waves either to the right or to the left.

If two of the four atoms or groups attached to carbon are identical, there is no asymmetry, and no optical activity. Thus, in a compound of the formula $CH_2X'Y'$, which we may represent by our tetrahedral scheme as shown in fig. 3, the two hydrogen atoms are equidistant from the carbon atom; the system has a plane of symmetry passing through X' Y' and the carbon atom, and has therefore a superposable mirror image.

If the molecule contains only one asymmetric carbon atom, the latter may be either positive or negative, so

that the substance may exist in two forms of opposite optical activity; in addition to which we may have the racemoid combination of the two, which will be inactive but separable. Mandelic acid, $C_6H_5.CH(OH).COOH$,* is a case in point: it is known in these three forms.

If, as in the case of tartaric acid, $\begin{matrix}CH(OH).COOH\\|\\CH(OH).COOH\end{matrix}$, the molecule contains two asymmetric carbon atoms, and at the same time consists of two structurally identical halves, then these two atoms may be either both positive or both negative, reinforcing each other's effect in either case; or one may be positive and the other negative, when, owing to the structural identity of the two halves of the molecule, the effect of the one will exactly compensate that of the other, and the compound will be inactive, but not separable. Furthermore, there may be the racemic combination of the bi-dextro form with the bi-lævo form—a combination inactive, but separable. We have thus the explanation of the four forms observed by Pasteur.

In fact all the complex cases of isomerism that have been met with among compounds of this class—compounds structurally identical, but configuratively distinct, as it is termed—may be satisfactorily explained, and their possible number accurately predicted, by means of the theory of the asymmetric carbon atom.

I must apologise to the organic chemists among my audience for inflicting on them this very elementary exposition of what to them is a well-known theory. But outside the circle of organic chemists the theory is, I fear, far from well known. Thus, an eminent physicist, in his "Theory of Light," referring to the rotation of the plane of polarisation by liquid or dissolved substances, says:—"I am not aware that any explanation of it has ever been suggested." And in the *Proceedings of the Royal Society* for the present year, another eminent physicist, after quoting with approval this purely personal confession, goes on to suggest the possibility of the molecules having a twisted structure, and points out that a right-handed twist "would appear right-handed when looked at from either end," apparently unaware that such conceptions have been commonplaces of stereochemistry for the past quarter of a century at least.

This brief sketch of the theory was therefore necessary in order that we may now effectively discuss Pasteur's views on the relation between optical activity and life.

Whenever we prepare artificially, starting either with the elements or with symmetric compounds, any organic compound which, when it occurs as a natural product of the living organism, is optically active, the primary product of our laboratory reactions, however closely it may in other respects resemble the natural product, differs from it in being optically inactive. Pasteur was greatly impressed by this fact. In the Lectures delivered in 1860 he says:—"Artificial products have no molecular asymmetry; and I could not point out the existence of any more profound distinction between the products formed under the influence of life, and all others." And again, he refers to "the molecular asymmetry of natural organic products," as "the great characteristic which establishes perhaps the only well-marked line of demarcation that can at present be drawn between the chemistry of dead matter and the chemistry of living matter." He would not admit that even racemoid forms, optically inactive by intermolecular compensation, might be artificially prepared; thus, to the suggestion that the malic acid which he had obtained from Dessaignes's artificial aspartic acid might possibly be the racemoid form (as we now know that it is), he replied:—"That is improbable, for then not only should we have made an active body from an inactive one, but we should have made two—a right and a left."

The view that racemoids could not be prepared artificially did not long remain tenable. In 1860, the year in which the foregoing lectures were delivered, Perkin and Duppa, and, independently, Kekulé, obtained from dibromsuccinic acid a form of tartaric acid, which Pasteur recognised as racemic acid. But the succinic acid employed had been prepared from amber, a substance of vegetable origin; and there was still the possibility that herein lay the source of the optical activity of the two constituents of the artificial racemic acid. This objection, which was raised by Pasteur himself, fell to the ground when, in 1873, Jungfleisch prepared racemic acid from Maxwell Simpson's synthetic succinic acid, and separated it into its right and left constituents by means of the sodium ammonium salt.

"Thus falls the barrier," wrote Schützenberger, "which M. Pasteur had placed between natural and artificial products. This example shows us how reserved we must be in attempting to draw distinctions between the chemical reactions of the living organism and those of the laboratory."

To these words, which, although written a quarter of a century ago, may fairly be taken as representing the prevailing belief of chemists at the present day, Pasteur replied as follows:

"Contrary to M. Schützenberger's belief this barrier still exists. . . . To transform *one inactive compound into another inactive compound* which has the power of resolving itself simultaneously into a right-handed compound and its opposite (*son symétrique*), is in no way comparable with the possibility of transforming *an inactive compound into a single active compound.* This is what no one has ever done; it is, on the other hand, what living nature is doing unceasingly before our eyes."

On this and subsequent occasions Pasteur did little more than reiterate opinions which he had previously expressed. As he himself stated, he was then occupied with other problems which absorbed his entire time and energies. The result has been that the opinions have suffered neglect and even misrepresentation. Thus Ostwald, in his *Allgemeine Chemie*, translating, or rather paraphrasing, the foregoing passage, omits the word "single"—which is the key to Pasteur's meaning—and then condemns the statement as illogical.

Pasteur's point is, that whereas living nature can make a *single* optically active compound, those laboratory reactions, to which we resort in synthesising such compounds, always produce, simultaneously, at least *two* of equal and opposite optical activity, the result being intermolecular compensation and consequent optical inactivity. Not necessarily implied in Pasteur's statement, but entirely in harmony with it, is the fact that we can sometimes produce artifically a single compound containing, within its molecule, two equal and opposite asymmetric groups, and therefore inactive by *intra*molecular compensation; thus in the oxidation of maleic acid to mesotartaric acid.

Let us consider the cause of this limitation of our synthetic reactions. Why cannot we produce, by laboratory processes, involving the play of symmetric forces and the interaction of symmetric atoms and molecules, *single* optically active compounds? To answer that question let us turn our attention to the mechanism of the change in which a symmetric carbon atom becomes asymmetric.

A simple case of such a change, typical of all similar changes, is the transformation of a compound, $CH_2X'Y'$, by substitution, into $CHX'Y'Z'$. If we follow this process by means of our tetrahedral model we see at once why, in our ordinary laboratory reactions, both enantiomorphs must be generated in equal quantity. The molecule of the compound, $CH_2X'Y'$, of which the tetrahedral representation is given in fig. 3, has, as we have already seen, a plane of symmetry passing through X'Y' and the carbon atom; and from this plane of symmetry the two hydrogen atoms are equidistant on opposite sides. Any purely mechanical, symmetric force, therefore—any force, for example, such as comes into play in the motions of the symmetric molecules of a gas or a liquid—which affects one of these hydrogen atoms in one molecule of the com-

* The asymmetric carbon atom is represented by an italic C.

pound $CH_2X'Y'$, has an equal chance of affecting the other hydrogen atom in another molecule. If the right-hand hydrogen atom in fig. 3 is replaced by the radicle Z', we obtain the enantiomorph represented in fig. 1; if the left-hand hydrogen atom, that represented in fig. 2. The chances in favour of these two events being equal, the ratio,

$$\frac{\text{Number of occurrences of event I.}}{\text{Number of occurrences of event II.}}$$

will, if we are dealing with an infinitely great number of molecules, approximate to unity. We therefore obtain a mixture, optically inactive by intermolecular compensation.

All cases of the conversion of symmetric into asymmetric compounds may be referred to the same category, no matter whether the chemical process is one of substitution or of addition, or whether the resulting molecule contains one or more asymmetric carbon atoms. Thus, in the reduction of a ketone of the formula $X'.CO.Y'$ to a secondary alcohol of the formula $X'.CH(OH).Y'$; in the transformation of an aldehyde by the addition of hydrocyanic acid into a nitrile of an α-hydroxy-acid; in the oxidation of fumaric acid to racemic acid—cases typifying the various additive processes in which asymmetric groupings are produced—there is one condition common to all: in the symmetric compound, with which we start, there are, in every case, two identical points of attack, equidistant from the plane of symmetry of the molecule, and the result is that the two possible events happen in equal number, so that the mixture of enantiomorphs obtained is optically inactive by compensation. We are, of course, in many cases able afterwards to separate these enantiomorphs by the methods devised by Pasteur, and thus obtain the single optically active compounds; but we cannot produce them singly as long as we have at our disposal only the symmetric forces which we command in the laboratory.

Precisely the same state of things prevails when symmetric molecules unite, under the influence of symmetric forces, to build up an asymmetric crystalline structure. When, for example, sodium chlorate crystallises from its aqueous solution, the number of right-handed crystals is, on the average, as was shown by Kipping and Pope, equal to the number of left-handed crystals. The same fact was proved by Landolt by observing the optical inactivity of the mixture of microscopic right and left crystals obtained by adding alcohol to a concentrated aqueous solution of sodium chlorate. The two possible asymmetric events occur in equal number.

Non-living, symmetric forces, therefore, acting on symmetric atoms or molecules, cannot produce asymmetry, since the simultaneous production of two opposite asymmetric halves is equivalent to the production of a symmetric whole, whether the two asymmetric halves be actually united in the same molecule, as in the case of mesotartaric acid, or whether they exist as separate molecules, as in the left and right constituents of racemic acid. In every case the symmetry of the whole is proved by its optical inactivity.

The result is entirely different, however, when we allow symmetric forces to act under the influence of already existing asymmetric, non-racemoid compounds.

Thus if we start with an optically active compound—a compound containing one or more asymmetric carbon atoms and non-racemoid—and, by appropriate chemical reactions, render asymmetric some carbon atom in the compound which was not previously so, then it does not follow that the two forms represented by the two possible arrangements of this new asymmetric carbon atom will be produced in equal quantity. The compound with which we start has no plane of symmetry; and, although there are still the two possible points of attack, one will be more exposed than the other; in fact, one mode of attack may so predominate that apparently only one asymmetric compound is formed, the other compound, if formed at all, escaping detection by the smallness of its amount. A case in point is the conversion of *d*-mannose by combination with hydrocyanic acid into the nitrile of *d*-mannoheptonic acid, studied by Emil Fischer, in which only one nitrile is formed, although there are two ways in which the hydrocyanic acid may attach itself to the aldehyde group of the mannose. On the other hand, the same general reaction, in the union of hydrocyanic acid with ordinary aldehyde $CH_3.CHO$—a symmetric compound—yields the right and left forms of lacto-nitrile $CH_3.CH(OH).CN$ in equal quantity, the two asymmetric events occurring in equal number, and the resulting mixture of compounds being inactive. It is the difference between guidance and no guidance: the asymmetric group present in the mannose guides into a particular path the symmetric forces which bring about the addition of the hydrocyanic acid; in the case of the symmetric aldehyde the result is left to pure chance. The latter action is like that of tossing a perfectly balanced coin; in the former the coin is heavily weighted on one side. The saying, "*les dés de la Nature sont pipés*," is certainly true of living nature and its products.

This guiding action displayed by asymmetric compounds may even impart a bias to the crystallisation of those molecularly symmetric substances already referred to, which crystallise in enantiomorphous forms. Thus Kipping and Pope have recently made the interesting observation that the crystals of sodium chlorate which are deposited from an aqueous solution containing 200 grms. of *d*-glucose to the litre consist, on an average, of about 32 per cent of right-handed to 68 per cent of left-handed crystals, the asymmetric carbohydrate, by its mere presence, favouring the formation of the one asymmetric form of the inorganic salt at the expense of the other.

(To be continued).

HYDROMETERS OF TOTAL IMMERSION.*

By A. W. WARRINGTON, M.Sc.

THE writer has made a series of experiments with the object of showing that the hydrometer becomes an instrument of scientific precision if it is modified so that when used it is totally immersed in the liquid.

Small ring-shaped platinum weights are slipped over the ungraduated neck of a glass hydrometer until the latter has nearly attained the specific gravity of the liquid to be tested. The temperature of the liquid is then slowly altered until the hydrometer and the liquid have exactly the same specific gravity.

With proper precautions this method gives results accurate to one in a million for temperatures from 0° to 40° C.

To determine the specific gravity of a solid use is made of a glass hydrometer of total immersion, which in form is not unlike a Nicholson hydrometer which has lost its tray. Two experiments are made at approximately the same temperature; in one of which the hydrometer is weighted only with pure mercury, and in the other it is weighted with the solid together with the necessary amount of mercury. As in the determination of the specific gravity of a liquid, the temperature is determined at which the hydrometer has no weight in water. The results are accurate to one in a hundred thousand.

An Honour.—Dr. A. B. Griffiths has been elected an Honorary Member of the Medical and Surgical Society of Rio Janeiro, Brazil, in recognition of his researches on the ptomaines.

* Abstract of a Paper read before the British Association (Section A), Bristol Meeting, 1898.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 107).

Alkalis.

The Lawrence Smith Method.— With the exception of a few determinations made in the early days of the Survey's existence, all alkali determinations have been made by the method of J. Lawrence Smith (*Am. Journ. Sci.*, 2nd series, vol. l., p. 269, 1871; *Am. Chemist*, vol. i., 1871; *Annalen Chem. und Pharm.*, vol. clix., p. 82, 1871), which is far more convenient than, and fully as accurate as, the older one, in which decomposition is effected by hydrofluoric and sulphuric acids. One of its chief advantages is the entire elimination of magnesia at the start.

The ammonium chloride used must be purified, preferably by sublimation, or by neutralising pure ammonia by pure hydrochloric acid, and the calcium carbonate is best obtained from pure calcite by solution and re-precipitation. However obtained, this last is not entirely free from alkalis, which must be estimated once for all in order to apply a correction. Eight grms. of the carbonate will contain usually from 0·0012 to 0·0016 grm. of alkaline chlorides, almost entirely the sodium salt, but the amount has been brought down to half the above by very long washing. This correction may be admitted at once to be a defect of the method, but it is one easily applied with safety.

The ignition may be made in a covered crucible of ordinary shape and of about 20 to 30 c.c. capacity, but the heat has to be kept so low in this case to avoid loss by volatilsation that perfect decomposition is not always assured. Hence, to avoid waste of time in very fine grinding, the form of crucible with cap, originally advocated by Smith, is very much to be preferred, since it permits, when set at an angle through an opening in the side of a fire-clay cylinder, of the application of the full heat of two burners, and perfect decomposition invariably results without the need of extraordinary care in grinding. The crucible used in this laboratory for ½ grm. of rock powder and 4 grms. calcium carbonate is 8 c.m. long, 1·8 c.m. wide at the mouth, and 1·5 at the bottom. For double the amounts or more the dimensions are 8 c.m., 2·5 c.m., and 2·2 c.m. The weights are 25 and 40 grms.

Perfectly satisfactory results are to be obtained with but a ½ grm. of rock powder. This is weighed out, ground down somewhat finer in a large agate mortar, mixed with its own weight of sublimed ammonium chloride, and the two thoroughly ground together. Then nearly all of 4 grms. of calcium carbonate is added, and the grinding continued till a thorough mixing has resulted. The contents of the mortar are transferred to the long crucible, the rest of the carbonate being used for rinsing off mortar and pestle. The crucible is then capped and placed in a clay cylinder, and heated for about ten minutes by a low, flat flame, placed at considerable distance beneath. As soon as the odour of ammonia is no longer perceptible the nearly full flame of two Bunsen burners is applied, and continued for forty to fifty minutes. The sintered cake detaches readily from the crucible as a rule; if not, it is softened up in a few minutes by hot water and digested in a dish until thoroughly disintegrated. It is first washed by decantation, and any lumps are broken up by a pestle, then thrown on the filter and well washed with hot water. The residue should dissolve completely in hydrochloric acid without showing the least trace of unattacked mineral.

The calcium is separated at once by ammonia and ammonium carbonate, and again after evaporation of the filtrate and expulsion of ammonium chloride. The weighed alkaline chlorides should be dissolved in water and filtered before addition of platinic chloride, in order to correct for the few hundredths of a m.grm. of fixed residue which is invariably left on the filter.

If the rock contains sulphur this will in part be found with the alkaline chlorides as sulphate. Therefore, if the sulphur is at all considerable in amount, it must be removed by barium chloride before the second precipitation by ammonium carbonate; otherwise there is danger of the potassium platinic chloride carrying sodium sulphate. A faint reaction for sulphate can usually be obtained, anyway, if the evaporations have been made on a water-bath fed by gas.

Lithium.—After separation of the potassium platinic chloride, the alcoholic filtrate is evaporated and tested spectroscopically for lithium. This element is almost invariably present, but almost never in amount to warrant quantitative estimation. Should it be so, however, the excellent Gooch method (*Proc. Am. Acad. Arts Sci.*, p. 177, 1886; *Bull. U.S. Geol. Survey*, No. 42, p. 73, 1887; Chemical News, vol. lv., pp. 18, 29, 40, 56, 78, 1887) of separation by amyl alcohol is to be followed, after removal of the platinum by hydrogen gas.* In rock analysis there need be no fear of enough lithium remaining with the potassium to cause any concern.

For the most accurate work it is still necessary to look for, and if possible estimate, the few hundredths of a m.grm. of calcium chloride that may be with the sodium chloride.

Carbon Dioxide.

For this estimation an apparatus permanently set up is used, of which several forms have been described by different writers. The rock powder is boiled with dilute hydrochloric acid in a small Erlenmeyer flask, attached to an upward-inclined condenser, whence, after passing through a compact arrangement of drying tubes—first, one of calcium chloride, then one of andydrous copper sulphate to retain hydrogen sulphide from decomposable sulphides and any hydrochloric acid that may pass over, and finally a second calcium chloride tube—the carbon dioxide is retained by absorption tubes filled with soda lime followed by calcium chloride. Of course arrangement is made for a current of CO_2-free air with which to sweep out the apparatus before and after the experiment, and for a slow current during its continuance. The results are very accurate, and the determination can be quickly carried out.

In the preliminary qualitative test for carbon dioxide, it must be remembered that while calcite gives off its carbon dioxide on treatment with cold acid, dolomite and siderite do not, and hence warming should not be omitted; otherwise, a few tenths per cent of carbon dioxide can very well be overlooked. Moreover, the powder should first be stirred up with a little hot water, to remove all entangled air which might otherwise appear to be carbon dioxide.

(To be continued).

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

* When haste is not an object, this way of removing platinum from the chlorides of the alkalis is by far the neatest and most satisfactory. The small flask containing the solution is placed in a water-bath and attached to a hydrogen generator. After expelling all air the flask is closed, without breaking connection with the generator, and left to itself, except for occasional light shaking up, till reduction is accomplished.

CORRESPONDENCE.

SCIENCE AND ART DEPARTMENT EXAMINATION.

To the Editor of the Chemical News.

Sir,—For more than twenty years I have annually sent pupils in for some of these examinations, and, although

at times unable to understand the reason for the adoption of some of the regulations, this is the first time that I have ever ventured to call attention to one or two points connected with the working of the Department. Recently, as is well known, the system of payment which has hitherto been adopted has been altered. It is claimed that this alteration is an improvement, because it is said to substitute payment by attendance for payment by results; but in reality it does nothing of the kind, for the examinational results are still one of the chief—if not *the* chief—factors in fixing the amount of grant. Also the amount of payment per attendance is so small that a most inadequate remuneration is given to the teacher. The result of this on the Science Classes throughout the country is that, while possibly only a comparatively slight alteration will be made in the total amount of money paid to large classes, such as the classes in large day-schools, the amount paid to smaller classes—especially those held in the evening where higher work is carried on—will be reduced to such an extent as to threaten the existence of many of them. For example, in a class known to me where work of the highest kind is carried on, and which work has been specially commended by the Inspector in two of his Annual Reports, the earnings this season will be reduced 75 per cent. If this is the outcome of the new policy, the sooner the Department reverts to the old plan the better for all concerned, and especially for the propagation of scientific knowledge.

Of course all teachers are aware of the anomalies which occur in examinations, but the following is a somewhat remarkable instance:—A student sat for the examination in May last in the Advanced Stage of Practical Organic Chemistry. He had to answer two questions and to analyse two substances (unknown), as well as to find the halogen element present in an organic solid and to determine the melting-point of this solid. The written questions were correctly answered, the analyses were correctly done, the halogen was correctly determined, and the melting-point of the substance was less than 1 per cent too low. The description of the practical work also was fairly well done; but this student is returned as having failed, notwithstanding that there are two classes of success—1st and 2nd class. It would be interesting to know, in the face of this, the standard the examiners require for a 1st class success. At the last May examinations the other chemistry results show many anomalies of a somewhat similar character.—I am, &c.,

D.Sc. (Lond.).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 23, June 6, 1898.

Yttric Earths contained in the Monazite Sands.—O. Boudouard.—Already inserted in full.

The Carbonic Acid of the Atmosphere.—MM. Albert-Lévy aud H. Henriet.—The authors have made a daily examination of the atmospheric carbonic acid for the last twenty years, and they show that the loss pointed out by M. Gautier due to what escapes from the potash is but a negligible quantity; they have always maintained that baryta is far the best absorbent of carbonic acid, and by making two estimations simultaneously with potash and baryta they have arrived at some very interesting results. On the outskirts of Paris they got practically the same results in each case, but in the city of Paris baryta gives a decidedly higher figure.

On a Crystallised Heptacetine, a Derivative of Ouabaine.—M. Arnaud.—250 grms. of pure acetic anhydride is used to dissolve 5 grms. of $ZnCl_2$; after cooling we add all at once 25 grms. of finely powdered anhydrous ouabaine (dried for 24 hours at 110°). Heat gently to about 30°—35° to help the reaction; the temperature suddenly and spontaneously rises to 70°—75°, the ouabaine is rapidly dissolved, and the solution takes a brown colour, becoming perfectly clear; if the temperature sinks below 60° the solution must be gently heated to bring it up to 70° again; finally, after cooling, it is poured into five or six times its volume of warm water. On standing the insoluble acetine is deposited in a crystalline mass, which can be purified by dissolving in boiling alcohol at 85°. The return of crystallised acetine is about 50 per cent of the ouabaine used, for at the same time a large proportion of amorphous acetine is formed soluble in alcohol and in other solvents. Crystallised acetine possesses the glucoside function and is a derivative of ouabaine and not a product of its splitting up. Analytical results show that heptacetine is formed by the dehydration of ouabaine, which by etherification gives heptacetine—

$$C_{30}H_{37}(C_2H_3O)_7O_{11}.$$

Some Acetals of Pyrocatechin.—Ch. Moureu.—Following up his research on pyrocatechin it occurred to the author to try what would be the action exerted on the acetal function by the free phenol function in the still unknown oxyacetal-phenol, and also whether the ortho-position of this latter would favour the reaction. He found that the influence of the free phenol function on the acetal function leads to the production of a mixed acetal with a closed hexagonal chain, this last compound being capable of opening its chain by hydration with the formation of the aldehyd corresponding to the primitive oxyacetal-phenol.

Nitration of Cellulose and of its Hydro- and Oxy-derivatives.—Leo Vignon.—The author has submitted pure cotton cellulose and the hydro- and oxy-celluloses to nitration. The nitration was pushed to its maximum, so as to decide whether the number of etherifiable hydroxyls of the cellulose had undergone any modification by its transformation into hydro- and oxy-cellulose. Ten grms. of dried cellulose, hydrocellulose, and oxycellulose were immersed respectively in 150 c.c. of a mixture of—

H_2SO_4, density 1·84.. .. .. 3 parts
HNO_3, ,, 1·50.. .. .. 1 part

The temperature was kept at 10° for twenty-four hours; the substance was then precipitated in two litres of cold water, washed till neutral, dried, and weighed; practically equal weights of the three substances were obtained—14 grms. to 16 grms. These nitrated products are inflammable; when kept in air the nitrated hydrocellulose becomes yellow and decomposes; so does the nitrated oxycellulose, but more slowly, while the nitrocellulose remains stable. The author concludes that cellulose, in its transformation into hydro- and oxy-cellulose, has not undergone any considerable change in the elementary structure of its original chemical type. It has, so to say, only been subjected to partial modifications, which form the subject of further research.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following information was received too late for insertion in the "Students' Number":—

Sheffield Technical School (University College, Technical Department).—Professor of Metallurgy, J. O. Arnold; Lecturer, A. McWilliam, A.R.S.M.; Demonstrator and Lecturer on Fuel, F. K. Knowles; Lecturer in Chemistry, F. Ibbotson, B.Sc., F.C.S. The work is di-

vided into two departments:—I. The Technical Department of the University College, including Mechanical, Electrical, Civil, and Mining Engineering; Metallurgy. II. The Evening Department, for providing Technical Instruction for persons engaged during the day in the local industries. The courses of Evening instruction include Magnetism and Electricity, Inorganic Chemistry, Experimental Laboratory, and Electrical Engineering. The Metallurgical Department has been equipped with a view to thoroughly meeting the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a new laboratory for the study of the micrographic analysis of metals has been completed and fully equipped with specially designed microscopes, by Ross, polishing tables, driven by an electric motor, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of steel. Special attention is given to the determination of the microscopic constituents of steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses and pass the necessary examinations. The course of study is as follows:—Preparatory Chemistry, Metallurgy Lectures, Fuel Lectures, Practical Metallurgy, Practical Fuel Course, Geology and Mineralogy, and Electro-Metallurgy.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Bristol Meeting of the British Association:—

President—Professor F. R. Japp, F.R.S.

Vice-Presidents—W. Shenstone, F.R.S.; Professor E. Noelting; A. Vernon Harcourt, F.R.S.; J. H. Gladstone, F.R.S.; Professor W. Ramsay, F.R.S.; Professor Emerson Reynolds, F.R.S.; W. J. Russell, F.R.S.

Secretaries—C. A. Kohn (Recorder); F. Wallis Stoddart; T. K. Rose.

Committee—Professor H. E. Armstrong, F.R.S.; The Earl of Berkeley; C. H. Bothamley; Professor Clowes; Sir William Crookes, F.R.S.; Professor H. B. Dixon, F.R.S.; R. G. Durrant; W. J. Elliot; T. Fairley; F. Francis; G. Gladstone; Herbert Jackson; H. C. Jenkins; A. P. Laurie; C. H. Luxmoore; H. G. Madan; Hugh Marshall; Professor McLeod, F.R.S.; Professor Meldola, F.R.S.; H. Forster Morley; D. H. Nagel; A. C. Pass; H. Ramage; S. Rideal; Professor Roberts-Austen, F.R.S.; Professor Smithells; Professor Lloyd Snape; J. Spiller: A. Stansfield; W. H. Symons; Morris Travers; T. Turner; G. Ward; Professor R. Warington, F.R.S.; Professor Wertheimer; Professor Sydney Young, F.R.S.

The Papers brought before the Section were as follows:—

President's Address.—Stereochemistry and Vitalism.

Prof. W. Ramsay and Dr. Morris W. Travers—On the Extraction from Air of the Companions of Argon and on Neon.

Prof. J. Emerson Reynolds—On the Position of Helium. Argon, Krypton, &c., in the Periodic Classification of the Elements.

Report of the Committee on the Electrolytic Methods of Quantitative Analysis.

Dr. Hugh Marshall—A New Form of Stand for Electrolytic Analysis.

Report of the Committee on the Continuation of th Bibliography of Spectroscopy.

Prof. Sydney Young—Some Researches on the Thermal Properties of Gases and Liquids.

Dr. W. J. Russell—The Action exerted by certain Metals and Organic Substances on a Photographic Plate.

Prof. P. F. Frankland—The Action of Bacteria on Photographic Plates.

Dr. J. H. Gladstone and Mr. Hibbert—Further Experiments on the Absorption of the Röntgen Rays by Chemical Compounds.

Report of the Committee on the Action of Light upon Dyed Colours.

H. P. Laurie and E. H. Strange—The Cooling Curves of Fatty Acids.

Earl of Berkeley—On the More Exact Determination of the Densities of Crystals.

Prof. F. Clowes—The Equivalent Replacement of Metals.

Prof. W. R. Hodgkinson and A. H. Coote—A Note on the Alkaline Chlorates and Sulphates of Heavy Metals.

Joint Discussion with Section A.—The Recent Eclipse Expeditions.

Report of the Committee on the Teaching of Natural Science in Elementary Schools.

Prof. H. E. Armstrong—Juvenile Research.

R. G. Durrant—Green Cobaltic Compounds.

Dr. C. M. Luxmoore—The Analysis of Dorsetshire Soils.

Report of the Committee on the Carbohydrates of the Cereal Straws.

Report of the Committee on the Promotion of Agriculture.

Dr. J. G. Parker—Recent Advances in the Tanning Industry.

Prof. E. Noelting—A New Class of Colouring Matters; Amidated Aromatic Amidines.

J. H. Fenton and F. Jackson—The Oxidation of Glycerol in presence of Ferrous Iron.

Dr. R. S. Morrell and J. M. Croft—Action of Hydrogen Peroxide on Carbohydrates in presence of Iron Salts.

Prof. J. Emerson Reynolds—An Experiment illustrating the Effect on the Acetylene Flame of varying proportions of Carbon Dioxide in the Gas.

A. G. Vernon Harcourt—On a 10-candle Lamp to be used as a Standard of Light.

A. G. Vernon Harcourt—On a Convenient Form of Drying Tube.

Dr. S. Rideal—Standards of Purity for Sewage Effluents.

Prof. W. R. Hodgkinson and Capt. Owen—Action of Ammonia on Gun-cotton.

J. A. Smythe—Nitroso-pinene.

J. B. Wood, W. H. Spivey, and T. H. Easterfield—The Constitution of Oxycannabin.

C. H. Bothamley—The Action of certain Substances on the Undeveloped Photographic Image.

Report of the Committee on Preparing a New Series of Wave-length Tables of the Spectra of the Elements.

Report of the Committee on Isomeric Naphthalene Derivatives.

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Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896). Alfred Jörgensen, "Micro-Organisms and Fermentation," London (F. W. Lyon), 1893.

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Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

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Note.—*The Entrance Examination for Intending Associates will be held on the First Day of the Session. Subjects:—Mathematics and Elementary Practical Geometry.*

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THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2026.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

BRISTOL, 1898.

By Professor F. R. JAPP, M.A., LL.D., F.R.S., President of the Section.

(Concluded from p. 144).

THESE observations possibly afford a clue to the mode of action of the living organism in producing single enantiomorphs. This production of single asymmetric forms may be a result of the asymmetric character of the chemical compounds of which the tissues of plants and animals are built up. The optically active products of the organism—the carbohydrates, the terpenes, tartaric acid, asparagine, quinine, the serum of the blood, and countless others—have been formed in an asymmetric environment, and their asymmetry is an induced phenomenon. They have been cast, as it were, in an asymmetric mould. According to this view they are a result of the selective production of one of the two possible enantiomorphous forms. The same would hold good with regard to the organised tissues themselves, developed from inherited asymmetric beginnings in the ovum or the seed, or obtained by fission. The perplexing question of the *absolute origin* of these asymmetric compounds I will discuss later.

Another view has been put forward by Emil Fischer. In his lecture on "Syntheses in the Sugar Group," delivered before the German Chemical Society in 1890, he says:—

"Starting with formaldehyd, chemical synthesis leads, in the first instance, to the optically inactive acrose. In contradistinction to this only the active sugars of the *d*-mannitol series have hitherto been found in plants.

"Are these the only products of assimilation [of carbon dioxide and water]? Is the preparation of optically active substances a prerogative of the living organism; is a special cause, a kind of vital force, at work here? I do not think so, and incline rather to the view that it is only the imperfection of our knowledge which imports into this process the appearance of the miraculous.

"No fact hitherto known speaks against the view that the plant, like chemical synthesis, first prepares the inactive sugars; that it then resolves them into their active constituents, using the members of the *d*-mannitol series in building up starch, cellulose, inulin, &c., whilst the optical isomerides serve for other purposes at present unknown to us."

There are, therefore, two opposite processes which would account for the presence of optically active compounds among the substances generated in the living organism, and which we may briefly describe as *selective production* and *selective consumption*. An instance of artificial selective production is the formation of only one nitrile of *d*-mannoheptonic acid already cited. Selective consumption, dissociated, however, from the previous production of the racemoid form, may be illustrated by the fermentation of dextro-tartaric acid in the action, studied by Pasteur and already referred to, of a mould on racemic acid, the lævo-tartaric acid remaining untouched, and by numerous similar fermentations since discovered. Selective consumption is not restricted to living ferments; various cases are known of enzymes, or soluble ferments, which can effect the hydrolysis of one glucoside, but not of its enantiomorph. As Emil Fischer, who studied this phenomenon, says:—"Enzyme and glucoside must fit each other like key and lock, in order that the one may exercise a chemical action on the other." And a similar selective action, embracing the much more complex phenomenon of alcoholic fermentation, is displayed by E. Buchner's soluble zymase obtained from yeast cells.

It is true, moreover, that the organism sometimes produces both enantiomorphs. Thus the lactic ferment converts carbohydrates into racemoid lactic acid; ordinary, or lævo-rotatory, asparagine is accompanied in plants, as Piutti showed, by a small quantity of its optical isomeride; and there are other cases.

These facts might be taken as evidence in favour of Fischer's view that selective consumption is the cause of the phenomenon we are discussing. But I do not think that, in the present state of our knowledge, we can decide between the two views. For that matter both may be correct, each may explain particular cases. What I wish to point out is that Fischer's statement that the "miraculous" character of the phenomenon is eliminated by his assumption appears open to question. It is just as much, or as little, miraculous after as before. The production of a single asymmetric form, and the destruction of one of two opposite asymmetric forms, are problems of precisely the same order of difficulty, and there are only two ways in which either of them have ever been solved; firstly, by the direct action of living matter, and, secondly, by the use of previously existing asymmetric non-racemoid compounds, which are, in the last resort, due to the action of life. Directly, or indirectly, then, life intervenes.

Doubtless this will appear a very extraordinary statement in view of Jungfleisch's synthesis of racemic acid and its re-solution into dextro- and lævo-tartaric acids by the crystallisation of the sodium ammonium salts. The process does not take place in a living organism; nor is the aid of life invoked in the shape of a micro-organism as in Pasteur's third method of separation. No asymmetric base of vegetable origin is employed as in Pasteur's second method, so that the indirect action of life through its products is also excluded; sodium and ammonium are symmetric inorganic radicles, and no substance of one-sided asymmetry is introduced from beginning to end. The process is one of ordinary crystallisation: the two forms are deposited side by side, the operator afterwards picking out the right and left crystals and separating them. The reason why the two tartrates crystallise out and not the racemate, is that at the ordinary temperature of the air at which the crystallisation is conducted they are less soluble than the racemate. At a higher temperature, on the other hand, these solubilities are reversed and the racemate is deposited. The conditions are precisely those which govern the formation or non-formation of ordinary double salts.

Consequently the overwhelming majority of chemists hold that the foregoing synthesis and separation of optically active compounds have been effected without the intervention of life, either directly or indirectly. Every manual of stereochemistry emphasises this point.

I have already hinted that I hold a contrary opinion. I have held it for some time, but have not ventured to give public expression to it, except in lecturing to my students. I was deterred chiefly by the impression that I stood alone in my belief. I find, however, that this was a mistaken impression. In a lecture on "Pasteur as the Founder of Stereochemistry," which Professor Crum Brown delivered before the Franco-Scottish Society in July, , 1897, and which is published in the *Revue française d'Edimbourg*, he says, referring to the separation of enantiomorphs by crystallisation:—

"The question has often occurred to me: Do we here get rid of the action of a living organism? Is not the observation and deliberate choice by which a human being picks out the two kinds of crystals and places each in a vessel by itself the specific act of a living organism of a kind not altogether dissimilar to the selection made by *Penicillium glaucum*? But I do not insist on this, although I think it is not unworthy of consideration."

It is this question, so precisely posed by Professor Crum Brown, that I would discuss in detail. I think we shall find that the answer to it will be in the sense which he indicates. The action of life, which has been excluded during the previous stages of the process, is introduced the moment the operator begins to pick out the two enantiomorphs.

It will doubtless be objected that, if this is the case, there can be no such thing as a synthesis of a naturally occurring organic compound without the intervention of life, inasmuch as the synthetic process is always carried out by a living operator.

Here, however, we must draw an important distinction. In the great majority of the operations which we carry out in our laboratories—such as solution, fusion, vaporisation, oxidation, reduction and the like—we bring to bear upon matter symmetric forces only—forces of the same order as those involved in the chance motions of the molecules of a liquid or a gas. All such processes, therefore, might conceivably take place under purely chance conditions, without the aid of an operator at all. But there is another class of operations to which Pasteur first drew attention, those into which one-sided asymmetry enters, and which deal either with the production of a single enantiomorph, or with the destruction (or change) of one enantiomorph in a mixture of both, or with the separation of two enantiomorphs from one another. We have already seen that such processes are possible only under one-sided asymmetric influences, which may take the form either of the presence of an already existing enantiomorph, or of the action of a living organism, or of the free choice of an intelligent operator. They cannot conceivably occur through the chance play of symmetric forces.

We must, therefore, in classifying the actions of the intelligent operator, distinguish between those actions in which his services might conceivably be dispensed with altogether, and those in which his intelligence is the essential factor. To the former class belongs the carrying out of symmetric chemical reactions; to the latter, the separation of enantiomorphs.

Take the synthesis of formic acid—a symmetric compound—by the absorption of carbon monoxide by heated caustic alkali. Given a forest fire and such naturally occurring materials as limestone, sodium carbonate, and water, it would not be difficult to imagine a set of conditions under which a chance synthesis of sodium formate from inorganic materials might occur. I do not assert that the conditions would be particularly probable, still they would not be inconceivable. But the chance synthesis of the simplest optically active compound from inorganic materials is absolutely inconceivable. So also is the separation of two crystallised enantiomorphs under purely symmetric conditions.

The picking out of the two enantiomorphs is, moreover, to be distinguished from the process of similarly separating the crystals of two different non-enantiomorphous substances, although this distinction is commonly ignored by classing both processes together as *mechanical*, in opposition to *chemical* separations. In the case of the non-enantiomorphs there may be differences of solubility, of specific gravity and the like, so that other means of separation, involving only the play of symmetric forces, may be resorted to. Such a process may justly be regarded as "mechanical." But the two crystallised enantiomorphs, as we have seen, have the same solubility—at least in symmetric solvents, the same specific gravity, behave, in fact, in an indentical manner towards all symmetric forces, so that no separation by such means is feasible. It requires the living operator, whose intellect embraces the conception of opposite forms of asymmetry, to separate them. Such a process cannot, by any stretch of language, be termed "mechanical." Conscious selection here produces the same result as the unconscious selection exercised by the micro-organism, the enzyme, or the previously existing asymmetric compound.

I need not point out that if the operator chooses to bring about the separation by an asymmetric solvent, or some other asymmetric means, he is still making use of his conception of asymmetry. He merely effects his end indirectly instead of directly. But in either case he exercises a guiding power which is akin, in its results, to that of the living organism, and is entirely beyond the reach of the symmetric forces of inorganic nature.

In like manner it is not of the least consequence, for the purposes of the present argument, whether the micro-organism, with which we have compared the operator, acts directly in fermenting one of two enantiomorphs, or whether it acts indirectly by first preparing an asymmetric enzyme which displays this selective action. The contention, therefore, of E. Fischer, Buchner, and others, that the discovery of enzymes and zymases "has transferred the phenomena of fermentation from biological to purely chemical territory," is true only as regards the immediate process, and leaves intact the *vitalistic origin* of these phenomena.

We thus arrive at the conclusion that the production of single asymmetric compounds, or their isolation from the mixture of their enantiomorphs, is, as Pasteur firmly held, the prerogative of life. Only the living organism with its asymmetric tissues, or the asymmetric products of the living organism, or the living intelligence with its conception of asymmetry, can produce this result. Only asymmetry can beget asymmetry.

Is the failure to synthesise single asymmetric compounds without the intervention, either direct or indirect, of life, due to a permanent inability, or merely to a temporary disability which the progress of science may remove? Pasteur took the latter view, and suggested that the formation of chemical compounds in the magnetic field, or under the influence of circularly polarised light, would furnish a means of solving the problem; and van 't Hoff also thinks the latter method feasible. As regards magnetism Pasteur's suggestion was undoubtedly based on a misconception; the magnetic field has not an asymmetric structure; it is merely polar, since the rotation which it produces in the plane of polarisation of a ray of light changes sign with the direction of the field. As regards circularly polarised light I must confess to having doubts as to whether it can be regarded as an asymmetric phenomenon: the motion of the ether about the axis of the ray is circular, not spiral, and it is only by considering the difference of phase from point to point along the ray that the idea of a spiral can be evolved from it. In fact, are there such things as forces asymmetric in themselves? Is the geometrical conception of asymmetry applicable to dynamical phenomena at all, except in so far as these deal with asymmetric material structures, such as quartz crystals, or organic molecules containing asymmetric carbon atoms? But this is a question which I would submit to the judgment of mathematical physicists.

One thing is certain—namely, that all attempts to form optically active compounds under the influence of magnetism or circularly polarised light have hitherto signally failed. These forces do not distinguish between the two equally exposed points of attack which present themselves in the final stage of the transformation of a symmetric into an asymmetric carbon atom.

But even if such an asymmetric force could be discovered—a force which would enable us to synthesise a single enantiomorph—the process would not be free from the intervention of life. Such a force would necessarily be capable of acting in two opposite asymmetric senses; left to itself it would act impartially in either sense, producing, in the end, both enantiomorphs in equal amount. Only the free choice of the living operator could direct it consistently into one of its two possible channels.

I will briefly recapitulate the conclusions at which we have arrived. Non-living, symmetric matter—the matter of which the inorganic world is composed—interacting under the influence of symmetric forces to form asymmetric compounds, always yields either pairs of enantio-

morphous molecules (racemoid form), or pairs of enantiomorphous groups united within the molecule (meso-form), the result being, in either case, mutual compensation and consequent optical inactivity. The same will hold good of symmetric matter interacting under the influence of asymmetric forces (supposing that such forces exist), provided that the latter are left to produce their effect under conditions of pure chance.

If these conclusions are correct, as I believe they are, then the *absolute origin* of the compounds of one-sided asymmetry to be found in the living world is a mystery as profound as the absolute origin of life itself. The two phenomena are intimately connected, for, as we have seen, these symmetric compounds make their appearance with life, and are inseparable from it.

How, for example, could lævo-rotatory protein (or whatever the first asymmetric compound may have been) be spontaneously generated in a world of symmetric matter, and of forces which are either symmetric or, if asymmetric, are asymmetric in two opposite senses? What mechanism could account for such selective production? Or if, on the other hand, we suppose that dextro- and lævo-protein were simultaneously formed, what conditions of environment existing in such a world could account for the survival of the one form and the disappearance of the other? Natural selection leaves us in the lurch here, for selective consumption is, under these conditions, as inconceivable as selective production.

No fortuitous concourse of atoms, even with all eternity for them to clash and combine in, could compass this feat of the formation of the first optically active organic compound. Coincidence is excluded, and every purely mechanical explanation of the phenomenon must necessarily fail.

I see no escape from the conclusion that, at the moment when life first arose, a directive force came into play—a force of precisely the same character as that which enables the intelligent operator, by the exercise of his Will, to select one crystallised enantiomorph and reject its asymmetric opposite.

I would emphasise the fact that the operation of a directive force of this nature does not involve a violation of the law of the conservation of energy. Enantiomorphs have the same heat of formation; the heat of transformation of one form into the other is nil. Whether, therefore, one enantiomorph alone is formed, or its optical opposite alone, or a mixture of both, the energy required per unit weight of substance is the same. There will be no dishonoured drafts on the unalterable fund of energy.

The interest of the phenomena of molecular asymmetry from the point of view of the biologist lies in the fact that they reduce to its simplest issues the question of the possibility or impossibility of living matter originating from dead matter by a purely mechanical process. They reduce it to a question of solid geometry and elementary dynamics; and therefore if the attempted mechanical explanation leads to a *reductio ad absurdum*, this ought to be of a correspondingly simple and convincing character. Let us see how far this is the case.

Life is a phenomenon of bewildering complexity. But in discussing the problem of the origin of life, this complexity cuts two ways. Whilst, on the one hand, it is appealed to by one set of disputants as an argument against the mechanical theory, on the other it affords shelter for the most unproved statements of their opponents. I will take a concrete instance from the writings of an upholder of the mechanical theory of the origin of life, the late Professor W. K. Clifford. He says:

"Those persons who believe that living matter, such as protein, arises out of non-living matter in the sea, suppose that it is formed like all other chemical compounds. That is to say it originates in a coincidence, and is preserved by natural selection. . . . The coincidence involved in the formation of a molecule so complex as to be called *living* must be, so far as we can make out, a very elaborate coincidence. But how often does it happen in a cubic mile of sea water? Perhaps once a week; perhaps once in many centuries; perhaps, also, many million times a day. From this living molecule to a speck of protoplasm visible in the microscope is a very far cry; involving, it may be, a thousand years or so of evolution."

It was easy for Clifford to write thus concerning life itself, for it was difficult for any one to contradict him. But had he been asked whether any mechanical (symmetric) coincidence would suffice to convert an infinitely great number of molecules of the type shown in fig. 3 into that shown in (say) fig. 1, to the exclusion of that shown in fig. 2; or whether, given a mixture, in equal proportions, of molecules of the types shown in figs. 1 and 2, any mechanical (symmetric) conditions of environment would bring about the destruction of one kind and the survival of the other, I think his exact mathematical and dynamical knowledge would have prevented him from giving an affirmative answer. But short of this affirmative answer, his other statements, it seems to me, fall to the ground.

I am convinced that the tenacity with which Pasteur fought against the doctrine of spontaneous generation was not unconnected with his belief that chemical compounds of one-sided asymmetry could not arise save under the influence of life.

Should any one object that the doctrine of the asymmetric carbon atom is a somewhat hypothetical foundation on which to build such a superstructure of argument as the foregoing, I would point out that the argument is in reality independent of this doctrine. All that I have said regarding the *molecular* asymmetry of naturally occurring optically active organic compounds, and all the geometrical considerations based thereon, hold good equally of the hemihedral *crystalline* forms of these compounds, about which there is no hypothesis at all. The production of a compound crystallising in one hemihedral form to the exclusion of the opposite hemihedral form, as in the case of the tartaric acid of the grape, is a phenomenon inexplicable on the assumption that merely mechanical, symmetric forces are at work. Nor is this conclusion invalidated even if we ultimately have to admit that the connection between molecular and crystalline asymmetry is not an invariable one—a point about which there is some dispute.

At the close of the lectures from which I have so frequently quoted, Pasteur, with full confidence in the importance of his work, but without any trace of personal vanity, says:—

"It is the theory of molecular asymmetry that we have just established—one of the most exalted chapters of science. It was completely unforeseen, and opens to physiology new horizons, distant but sure."

I must leave physiologists to judge how far they have availed themselves of the new outlook which Pasteur opened up to them. But if I have in any way cleared the view towards one of these horizons, I shall feel that I have not occupied this chair in vain.

Some of my hearers, however, may think that, instead of rendering the subject clearer, I have brought it perilously near to the obscure region of metaphysics; and certainly, if to argue the insufficiency of the mechanical explanation of a phenomenon is to be metaphysical, I must plead guilty to the charge. I will, therefore, appeal to a judgment—metaphysical, it is true, but to be found in a very exact treatise on physical science—namely, Newton's "Principia." It has a marked bearing on the subject in hand:—

"*A cæca necessitate metaphysica, quæ utique eadem est semper et ubique, nulla oritur rerum variatio.*"

I will merely add that this is certainly true of the particular *rerum variatio* in which optically active organic compounds originate.

ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION.

BRISTOL, 1898.

By Professor W. E. AYRTON, F.R.S., President of the Section.

A YEAR ago Section A was charmed with a Presidential Address on the poetry of mathematics, and if, amongst those who entered the Physics lecture theatre at Toronto on that occasion, there were any who had a preconceived notion that mathematics was a hard, dry, repellent type of study, they must, after hearing Professor Forsyth's eloquent vindication of its charms, have departed convinced that mathematics resembled music in being a branch of the fine arts. Such an address, however, cannot but leave a feeling of regret amongst those of us who engulfed in the whirl of the practical science of the day, sigh for the leisure and the quiet which are necessary for the worship of abstract mathematical truth, while the vain effort to follow in the footsteps of one gifted with such winning eloquence fills me with hopeless despair.

Section A this year is very fortunate in having its meetings associated with those of an "International Conference on Terrestrial Magnetism and Atmospheric Electricity," which is attended by the members of the "Permanent Committee for Terrestrial Magnetism and Atmospheric Electricity" of the "International Meteorological Conference." It has been arranged that this Permanent Committee, of which Professor Rücker is the President, shall form part of the General Committee of Section A, and also shall act as the Committee of the International Conference, which will itself constitute a separate department of Section A. For the purpose, however, of preparing a Report to the International Meteorological Conference, and for similar business, this Permanent Committee will act independently of the British Association.

My first duty to-day, therefore, consists in expressing the honour and the very great pleasure which I feel in bidding you, members of the International Conference, most heartily welcome.

Among the various subjects which it is probable that the Conference may desire to discuss, there is one to which I will briefly refer, as I am able to do so in a triple capacity. The earth is an object of much importance, alike to the terrestrial magnetician, the telegraph electrician, and the tramway engineer; but while the first aims at observing its magnetism, and the second rejoices in the absence of the earth currents which interfere with the sending of messages, the third seems bent on converting our maps of lines of force into maps of lines of tramway.

It might, therefore, seem as if electric traction—undoubtedly a great boon to the people, and one that has already effected important social developments in America and on the continent of Europe—were destined in time to annihilate magnetic observatories near towns, and even to seriously interfere with existing telegraph and telephone systems. Already the principle of the survival of the fittest is quoted by some electrical engineers, who declare that if magnetic observatories are crippled through the introduction of electric tramways, then so much the worse for the observatories. And I fear that my professional brethren only look at me askance for allowing my devotion to the practical applications of electricity to be tainted with a keen interest in that excessively small, but none the less extremely wonderful, magnetic force which controls our compass needles.

But this interest emboldens me to ask again, Can the system of electric traction that has already destroyed the two most important magnetic observatories in the United States and British North America be the best and the fittest to survive? Again, do we take such care, and spend such vast sums, in tending the weak and nursing the sick because we are convinced that they are the fittest to survive? May it not perhaps be because we have an inherent doubt about the justness of the survival of the strongest, or because even the strongest of us feels compelled to modestly confess his inability to pick out the fittest, that modern civilisation encourages *not* the destruction but the preservation of what has obvious weakness, on the chance that it may have unseen strength?

When the electrical engineer feels himself full of pride at the greatness, the importance, and the power of his industry, and when he is inclined to think slightingly of the deflection of a little magnet compared with the whirl of his 1000 horse-power dynamo, let him go and visit a certain dark store-room near the entrance hall of the Royal Institution, and, while he looks at some little coils there, ponder on the blaze of light that has been shed over the whole world from the dimly-lighted cupboard in which those dusty coils now lie. Then he may realise that while the earth as a magnet has endured for all time, the earth as a tramway conductor may at no distant date be relegated to the class of temporary makeshifts, and that the raids of the feudal baron into the agricultural fields of his neighbours were not more barbarous than the alarms and excursions of the tramway engineer into the magnetic fields of his friends.

A very important consideration in connection with the rapid development of physical inquiry is the possibility of extending our power of assimilating current physical knowledge. For so wide have grown the limits of each branch of physics that it has become necessary to resort to specialisation if we desire to widen further the region of the known. On the other hand, so interlinked are all sections of physics that this increase of specialisation is liable to hinder rather than assist advance of the highest order.

An experimenter is, therefore, on the horns of a dilemma—on the one hand, if he desires to do much he must confine himself more or less to one line of physical research, while, on the other hand, to follow that line with full success requires a knowledge of the progress that is being made along all kindred lines. Already an investigator who is much engaged with research can hardly do more as regards scientific literature than read what he himself writes—soon he will not have time to do even that. Division of labour and co-operation have, therefore, become as important in scientific work as in other lines of human activity. Like bees, some must gather material from the flowers that are springing up in various fields of research, while others must hatch new ideas. But, unlike bees, all can be of the "worker" class, since the presence of drones is unnecessary in the scientific hive.

Englishmen have long been at a disadvantage in not possessing any ready means of ascertaining what lines of physical inquiry were being pursued in foreign countries—or, indeed, even in their own. And, so far from making it easier to obtain this information, our countrymen have, I fear, until quite recently, been guilty of increasing the difficulty. For every college, every technical school in Great Britain—and their number will soon rival that of our villages—seems to feel it incumbent on itself to start a scientific society. And in accordance with the self-reliant character of our nation, each of these societies must be maintained in absolute independence of every other society, and its proceedings must be published separately, and in an entirely distinct form from those of any similar body. To keep abreast, then, with physical advance in our own country is distinctly difficult, while the impossibility of maintaining even a casual acquaintance with foreign scientific literature lays us open to a charge of international rudeness.

There is, of course, the German *Beiblätter*, but the

Anglo-Saxon race, which has spread itself over so vast a portion of the globe, is proverbially deficient in linguistic powers, and consequently, till quite recently, information that was accessible to our friends on the Continent was closed to many workers in Great Britain, America, and Australia.

Influenced by these considerations the Physical Society of London, in 1895, embarked on the publication of abstracts from foreign papers on pure physics, and, as it was found that this enterprise was much appreciated, the question arose at the end of the following year, whether, instead of limiting the journals from which abstracts were made to those appearing in foreign countries, and the papers abstracted to those dealing only with pure physics, the abstracts might not with advantage be enlarged, so as to present a *résumé* of all that was published in all languages on physics and its applications.

The first application of physics which it was thought should be included was electrical engineering, and so negotiations were opened with the Institution of Electrical Engineers. After much deliberation on the part of the representatives of the two societies, it was finally decided to start a monthly joint publication, under the management of a committee of seven, two of whom should represent the Institution of Electrical Engineers, two the Physical Society, and three the two societies jointly. *Science Abstracts* was the name selected for the periodical, and the first number appeared in January of this year.

A section is devoted to general physics, and a separate section to each of its branches; similarly a section is devoted to general electrical engineering, and a separate section to each of its more important subdivisions. The value of *Science Abstracts* is already recognised by the British Association as well as by the Institution of Civil Engineers, for those societies make a liberal contribution towards the expenses of publication, for which the Physical Society and the Institution of Electrical Engineers are responsible.

At no distant date it is thought that other bodies may co-operate with us, and we have hopes that finally the scheme may be supported by the scientific societies of many Anglo-Saxon countries. For our aim is to produce, in a single journal, a monthly record in English of the most important literature appearing in all languages on physics and its many applications. This is the programme—a far wider one, be it observed, than that of the *Beiblätter*—which we sanguinely hope our young infant *Science Abstracts* will grow to carry out.

The saving of time and trouble that will be effected by the publication of such a journal can hardly be overestimated, and the relief experienced in turning to a single periodical for knowledge that could hitherto be obtained solely by going through innumerable scientific newspapers, in many different languages, can only be compared with the sensation of rousing from a distracting and entangled dream to the peaceful order of wakeful reality.

I therefore take this opportunity of urging on the members of the British Association the importance of the service which they can individually render to science by helping on an enterprise that has been started solely in its aid, and not for commercial purposes.

The greatness of the debt owed by industry to pure science is often impressed on us, and it is pointed out that the comparatively small encouragement given by our nation to the development of pure science is wholly incommensurate with the gratitude which it ought to feel for the commercial benefits science has enabled it to reach. This is undoubtedly true, and no one appreciates more fully than myself how much commerce is indebted to those whose researches have brought them—it may be fame, but certainly nothing else. The world, however, appears to regard as equitable the division of reward which metes out tardy approbation to the discoverer for devising some new principle, a modicum of the world's goods to the inventor for showing how this principle can be applied, and a shower of wealth on the contractor for putting the principle into practice. At first sight this appears like the irony of fate, but in fact the world thus only proves that it is human by prizing the acquisition of what it realises that it stands in need of, and by valuing the possession of what it is able to comprehend.

Now is there not a debt which those who pursue pure science are in their turn equally forgetful of—viz., the debt to the technical worker or to some technical operation for the inception of a new idea? For purely theoretical investigations are often born of technics, or, as Whewell puts it, "Art is the parent, not the progeny, of science; the realisation of principles in practice forms part of the prelude as well as of the sequel of theoretical discovery." I need not remind you that the whole science of floating bodies is said to have sprung from the solution by Archimedes of Hiero's doubt concerning the transmutation of metals in the manufacture of his crown. In that case, however, it was the transmutation of gold into silver, and not silver into gold, that troubled the philosopher.

Again, in the "History of the Royal Society at the End of the Eighteenth Century," Thomson says regarding Newton, "A desire to know whether there was anything in judicial astrology first put him upon studying mathematics. He discovered the emptiness of that study as soon as he erected a figure; for which purpose he made use of one or two problems in Euclid. . . . . He did not then read the rest, looking upon it as a book containing only plain and obvious things."

The analytical investigation of the motion of one body round an attracting centre, when disturbed by the attraction of another, was attacked independently by Clairault, D'Alembert, and Euler, because the construction of lunar tables had such a practical importance, and because large money prizes were offered for their accurate determination.

The gambling table gave us the whole Theory of Probability, Bernoulli's and Euler's theorems, and the first demonstration of the binomial theorem, while a request made to Montmort to determine the advantage to the banker in the game of "pharaon" started him on the consideration of how counters could be thrown, and so led him to prove the multinomial and various other algebraical theorems. Lastly, may not the gambler take some credit to himself for the first suggestion of the method of least squares, and the first discussion of the integration of partial differential equations with finite differences contained in Laplace's famous "Théorie Analytique des Probabilités"?

The question asked Rankine by James R. Napier regarding the horse-power which would be necessary to propel, at a given rate, a vessel which Napier was about to build, resulted in the many theoretical investigations carried out by Rankine on water lines, skin-friction, stream lines, &c. For, as Professor Tait has said, "Rankine, by his education as a practical engineer, was eminently qualified to recognise the problems of which the solution is required in practice; but the large scope of his mind would not allow him to be content with giving merely the solution of those particular cases which most frequently occur in engineering as we now know it. His method invariably is to state the problem in a very general form, find the solution, and apply this solution to special cases."

Helmholtz studied physiology because he desired to be a doctor, then physics because he found that he needed it for attacking physiological problems, and lastly mathematics as an aid to physical research. But I need not remind you that it is his splendid work in mathematics, physics, and physiology, and not his success in ministering to the sick, that has rendered his name immortal.

Did not Kepler ask "How many would be able to make astronomy their business if men did not cherish the hope of reading the future in the skies?" And did he not

warn those who objected to the degradation of mingling astrology with astronomy, to beware of "throwing away the child with the dirty water of its bath"? Even now, may we not consider all the astronomical research work done at the Royal Observatory, Greenwich, as a by-product, since the Observatory is officially maintained merely for the purposes of navigation? And are there not many of us who feel assured that, since researches in pure physics and the elucidation of new physical facts must quite legitimately spring from routine standardising work, the most direct way—even now at the end of the nineteenth century—of securing for the country a National Physical Laboratory is to speed forward a Government standardising institute?

Lastly, as you will find in Dr. Thorpe's fascinating "Life of Davy," it was the attempt to discover the medicinal effect of gases at the Pneumatic Institution in this city that opened up to Davy the charm of scientific research. And, indeed, the Royal Institution itself, the scientific home of Davy, Faraday, Tyndall, Rayleigh, and Dewar, owes its origin to Romford's proposal "for forming in London by private subscription an establishment for feeding the poor and giving them useful employment . . . connected with an institution for introducing and bringing forward into general use new inventions and improvements by which domestic comfort and economy may be promoted."

(To be continued).

ON THE EXTRACTION OF THE COMPANIONS OF ARGON AND ON NEON.*

By WILLIAM RAMSAY, F.R.S., and MORRIS W. TRAVERS.

In the Presidential Address to the Chemical Section of this Association, delivered last year at Toronto, it was pointed out that the densities of helium and argon being respectively 2 and 20 in round numbers, and the ratio of their specific heats being in each case 1·66, their atomic weights must be respectively 4 and 40. If the very probable assumption is made that they belong to the same group of elements, it appears almost certain on the basis of the Periodic Table that another element should exist, having an atomic weight higher than that of helium by about 16 units, and lower than that of argon by about 20. There is also room for elements of higher atomic weight than argon, belonging to the same series. The search for this element was described in last year's Address, and, it will be remembered, the results were negative.

Reading between the lines of the Address, an attentive critic might have noticed that no reference was made to the supposed homogeneity of argon. From speculations of Dr. Johnstone Stoney, it would follow that the atmosphere of our planet might be expected to contain new gases, if such exist at all, with densities higher than 8 or thereabouts. Dr. Stoney gives his reasons for supposing that the lighter the gas the less its quantity in our atmosphere, always assuming that no chemical compounds are known which would retain it on the earth, or modify its relative amount. Therefore it appeared worthy of inquiry whether it was possible to separate light and also heavy gases from argon.

The beautiful machine invented by Dr. Hampson has put it in our power to obtain, through his kindness and that of the "Brin" Oxygen Company, large quantities of liquid air. We were therefore able to avail ourselves of the plan of liquefaction, and subsequent fractional distillation, in order to separate the gases.

On liquefying 18 litres of argon, and boiling off the first fraction, a gas was obtained of density 17 (o=16). This gas was again liquefied and boiled off in six fractions. The density of the lightest fraction was thus reduced to 13·4, and it showed a spectrum rich in red, orange, and yellow lines, differing totally from that of argon. On refractionating, the density was reduced further to 10·8; the gas still contained a little nitrogen, on removing which the density decreased to 9·76. This gas is no longer liquefiable at the temperature of air boiling under a pressure of about 10 m.m.; but if, after compression to two atmospheres, the pressure was suddenly reduced to about a quarter of an atmosphere, a slight mist was visible in the interior of the bulb. This gas must necessarily have contained argon, the presence of which would obviously increase its density; and in order to form some estimate of its true density, some estimate must be made of the relative amount of the argon. We have to consider a mixture of neon, nitrogen, and argon, the two latter of which are capable, not merely of being liquefied, but of being solidified without difficulty. Under atmospheric pressure nitrogen boils at $-194°$, and solidifies at $-214°$, and the boiling-point of argon is $-187°$, and the freezing-point $-190°$; the vapour-pressure of nitrogen is therefore considerably higher than that of argon. The mist produced on sudden expansion consisted of solid nitrogen and argon; and for want of better knowledge, assuming the vapour-pressure of the mixture of nitrogen and argon to be the sum of the partial pressures of the two, it is obvious that that of argon would form but a small fraction of the whole. The vapour-pressure of argon was found experimentally to be 109 m.m. at the temperature of air boiling in as good a vacuum as could be produced by our pump; but as we have only to consider the partial pressure of the argon at a much lower temperature, we do not believe that the pressure of the argon can exceed 10 m.m. in the gas. This would correspond to a density for neon of 9·6.

The ratio between the specific heat at constant pressure and constant volume was determined in the usual way for neon, and, as was to be expected, it approximates closely to the theoretical ratio, being 1·655. We therefore conclude that, like helium and argon, the gas is monatomic.

It may be remembered that the refractivity of helium compared with that of air is exceptionally low—viz., 0·1238. The lighter gas, hydrogen, has a refractivity of 0·4733. It was to be expected from the monatomic character and low density of neon that its refractivity should be also low; this expectation has been realised, for the number found is 0·3071. Argon, on the other hand, has a refractivity not differing much from that of air—viz., 0·958. Since the sample of neon certainly contains a small amount of argon, its true refractivity is probably somewhat lower. Experiments will be carried out later to ascertain whether neon resembles helium in its too rapid rate of diffusion.

The spectrum of neon is characterised by brilliant lines in the red, the orange, and the yellow. The lines in the blue and violet are few, and comparatively inconspicuous. There is, however, a line in the green, of approximate wave-length 5030, and another of about 5400.

A few words may be said on the other companions of argon. The last fractions of liquefied argon show the presence of three new gases. These are krypton, a gas first separated from atmospheric air, and characterised by two very brilliant lines, one in the yellow and one in the green, besides fainter lines in the red and orange; metargon, a gas which shows a spectrum very closely resembling that of carbon monoxide, but characterised by its inertness, for it is not changed by sparking with oxygen in presence of caustic potash; and a still heavier gas, which we have not hitherto described, which we propose to name "xenon." Xenon is very easily separated, for it possesses a much higher boiling-point, and remains behind after the others have evaporated. This gas, which has been obtained practically free from krypton, argon, and metargon, possesses a spectrum

* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

analogous in character to that of argon, but differing entirely in the position of the lines. With the ordinary discharge the gas shows three lines in the red, and about five very brilliant lines in the blue; while with the jar and spark-gap these lines disappear, and are replaced by four brilliant lines in the green, intermediate in position between the two groups of argon lines, the glow in the tube changing from blue to green. Xenon appears to exist only in very minute quantity.

Indeed all of these gases are present only in small amount. It is, however, not possible to state with any degree of accuracy in what proportion they are present in atmospheric argon. Of neon, perhaps, we may say that the last fraction of the lightest 100 c.c. from 18 litres of atmospheric argon no longer shows the neon spectrum, and possesses the density of argon; it may be safe to conclude, therefore, that 18 litres of argon do not contain more than 50 c.c. of neon; the proportion of neon in air must therefore be about one part in 40,000. We should estimate the proportion of the heavy gases at even less.

It follows from these remarks that the density of argon is not materially changed by separating from it its companions. A sample of gas, collected when about half the liquid argon or about 10 c.c. had boiled off, possessed the density 19·89; the density of atmospheric argon is 19·94. But, of course, we give this density of argon as only provisional (July 30, 1898); for a final determination the density must be determined after more thorough fractionation.

With a density of 9·6, and a consequent atomic weight of 19·2, neon would follow fluorine and precede sodium in the Periodic Table; as to the other gases, further research will be required to determine what position they hold.

EQUIVALENT REPLACEMENT OF METALS.*

By Professor FRANK CLOWES, D.Sc. (Lond.).

It has long been known that when iron is immersed in a solution of cupric sulphate metallic copper is deposited, and an amount of iron passes into solution which is exactly able to combine with the sulphate radicle liberated from the cupric sulphate. The weights of copper and of iron which combine with the same weight of sulphate radicle have been determined by carrying out the process quantitatively. These weights are chemically equivalent to one another, for they are able to combine with the same weight of the acidulous radicle.

In the case just cited, the chemical change appears at ordinary temperature and with dilute cupric solution, to follow the simple course stated. But attempts to extend this direct method of ascertaining the relative equivalents of metals cease to be direct in certain cases, owing to the complicated nature of the reactions which occur.

My attention was drawn to such a complication in the case of the action of magnesium on cupric sulphate solution, and the nature of the reaction was then investigated by R. M. Caven, B.Sc., and myself. Commaille (*Comptes Rendus*, lxiii., p. 556), Kern (Chem. News, xxxiii., p. 236), and Vitali (*Journ. Chem. Soc.*, lxx., 419), had drawn attention to the facts that during the action of magnesium on cupric sulphate solution cuprous oxide was deposited with the metallic copper, and hydrogen was evolved. These facts prove that the copper equivalent of magnesium cannot be obtained by simply weighing the magnesium which passes into solution and the deposit which was formed during the process. But we proceeded to make a fuller examination of the nature of the reaction, and to show that when it was quantitatively carried out the products enabled us to calculate the equivalents of magnesium and copper.

* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

Having obtained practically pure materials, we proceeded to study the reactions when the conditions were varied by employing hot or cold and strong or weak cupric sulphate solutions. We were met with the initial difficulty that cupric sulphate solution deposits a basic salt when it is boiled: this salt we separated and found to correspond in composition and properties to the formula $4CuSO_4.7Cu(OH)_2.H_2O$. Pickering had separated a similar salt, to which he attributed the formula $6CuO.2SO_3.5H_2O$. Owing to the deposition of this salt complicating the products, we avoided actual ebullition in our experiments.

The action is most simple when the magnesium is immersed in a hot strong solution of cupric sulphate. Hydrogen is briskly evolved, a chocolate-coloured deposit forms, and green flakes are produced which disappear before the reaction is completed. Treatment of the brown deposit with dilute hydrochloric acid yields colourless cuprous chloride solution and a small residue of metallic copper. The hydrogen evolved was collected and measured, the metallic copper was weighed directly, and the amount of cuprous oxide was determined by dissolving it in hydrochloric acid and determining the amount of cuprous chloride thus formed by titrating it with standard permanganate solution in the presence of a sufficient amount of magnesium sulphate. As a result of four experiments the average sum of the magnesium equivalents of the cuprous oxide, the copper, and the hydrogen amounted to 0·102 grm., and the average weight of magnesium used was 0·105 grm. The ratios of the weights of hydrogen, copper, and cuprous oxide produced were constant only when the conditions of the experiment were precisely similar.

When the hot cupric sulphate is dilute, or when it is employed at ordinary temperature, the reaction pursues at first a similar course, but it soon becomes very considerably delayed by the formation of a green basic cupric salt, intermingled with colourless basic magnesium salt. Thus the reaction on the magnesium was usually complete in ten minutes in an excess of a hot strong solution of cupric sulphate; but in weak and cold solutions it often extended over several days, and even a week.

The percentage of hydrogen, compared with that which is equivalent to the magnesium employed, was in the case of the hot solution 34·7; with the cold solution it was 41·5 with weak solution, and 30·6 with saturated solution.

Various explanations have been given of the causes which lead to deposition of cuprous oxide and to evolution of hydrogen. It has been suggested that the change is due to impurity in the copper salt; this we have disproved by using a salt purified by frequent re-crystallisation, and yielding 25·23 per cent of copper (theory = 25·39); we have also proved the purity of the magnesium employed. Divers suggests that the evolution of hydrogen is due to the action of the magnesium upon free sulphuric acid, which has been formed by hydrolysis of the cupric salt. This seems to us to be an insufficient explanation of the rapidity with which hydrogen is evolved. Cold cupric sulphate solution was found to give no acid reaction with methyl-orange, although it is faintly acid to litmus paper. Yet such a solution gives an immediate evolution of hydrogen when magnesium is immersed in it, the evolution of the gas being very rapid in a hot and strong solution. After carefully studying the change, we are inclined to attribute the evolution of hydrogen in small degree to the presence of free sulphuric acid formed by hydrolysis in cold solution, and in greater degree to the same cause in hot solution. This involves the formation and separation of basic salt. This reaction, however, does not account for all the hydrogen evolved, and one of us will be prepared before long to advance a further explanation to account for this. Divers further suggests that cuprous sulphate is formed and almost immediately converted by the action of the basic cupric salt into cuprous oxide; this theory we also find to be untenable.

The immediate separation of cuprous oxide and evolution of hydrogen, without formation of basic salt, which occurs at the commencement of the reaction, may be represented by the equation—

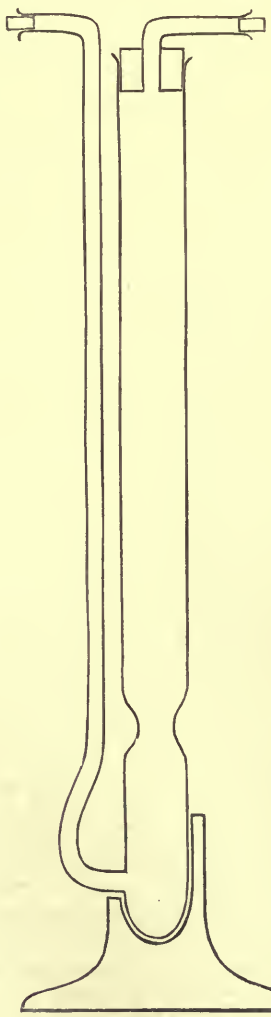
$$2Mg+2CuSO_4+H_2O=2MgSO_4+Cu_2O+H_2.$$

The action of the magnesium-copper couple has been proved to be too slow to explain the rapid escape of hydrogen, and if this were the origin of the hydrogen, its escape would not immediately follow the immersion of the magnesium.

ON A CONVENIENT FORM OF DRYING TUBE.*

By A. G. VERNON HARCOURT, F.R.S.

A COMMON method of drying gases is to pass them through a wash-bottle containing sulphuric acid and then through a U-tube filled with fragments of pumice moistened with the same liquid. The number of corks and connections



in this arrangement increase the chance of leakage. The U-tube must be supported in an upright position both when in use and afterwards, that the acid may not come in contact with the corks; if too much acid is poured in, the bend becomes blocked by a plug of liquid; there is no means of telling when the acid has become less efficient by dilution; nor is it easy to re-charge the tube with fresh acid.

The form of drying-tube shown avoids these defects. It is at once wash-bottle and drying-tube. It has one cork and stands upright; the pumice can be well drenched with sulphuric acid, the excess draining down and filling the lower part (through which the gas bubbles) to a convenient height; dilution announces itself, and the acid is easily renewed. The shape is that of a Gay-Lussac burette with a constriction about two inches from the bottom. A piece of pumice, large enough to block the constriction is first dropped in, and the tube is filled to near the top with small fragments of pumice. In charging with acid care is taken not to wet the upper part of the tube; next day the level of the acid in the lower part of the tube is marked with a strip of gummed paper. The small side tube which enters the large tube near the bottom is the inlet for gas; when the moisture absorbed has raised the level of the acid about 2 m.m. above the mark, the acid in the lower part is poured off through the small tube, and fresh acid is poured in through the pumice. The inlet and outlet tubes are made of the same height, so that a series of similar drying tubes may readily be joined together.

* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

ON THE LUMINOSITY PRODUCED BY STRIKING SUGAR.*

By JOHN BURKE, M.A.

WHEN two lumps of sugar are struck a flash is produced of a somewhat bluish white colour, but the light is instantaneous, and yet at the same time spreads into the sugar itself far beneath the struck surface. An almost continuous luminosity, however, has been produced by a hammer striking automatically the rim of a rapidly rotating wheel of sugar (obtained by cutting up a sugar-loaf into a number of discs); the wheels or discs being about an inch thick, so as to stand the violent hammering; the hammer, being of the nature of a pendulum about four feet in length, which was drawn aside by an electro-magnet and then let go. Curiously enough, if the impact is given when the wheel is stationary, so that only an impulse is given without rubbing, or if, on the other hand, the wheel is set spinning and the hammer is stationary and merely allowed to rub up against the wheel, the phenomenon is insignificantly small compared to that obtained when both rubbing and knocking take place together; that is, when the wheel and hammer are both working.

The spectrum of the luminosity is confined to the more refrangible end of the spectrum, commencing somewhere about F, but it is difficult to say exactly.

One difficulty in the way of observing the spectrum—and still more of photographing it—is the rapid rate at which this sugar wears out; and to overcome this the whole apparatus is fixed on rollers moved slowly along at a suitable rate to compensate for the change in the position of the sparks which would otherwise take place, and by this means the sparks or flashes of luminosity, which appear almost continuous, are made to take place always along the axis of the collimator of the spectroscope.

The fact that the less refrangible part of the spectrum is absent shows undoubtedly that the luminosity cannot be due to the particles of sugar becoming red-hot or white-hot by the impacts, but seems to show that the light produced is due either to some change in the configuration of the crystals of sugar or to some sort of chemical action

* Abstract of a Paper read before the British Association (Section A), Bristol Meeting, 1898.

set up between the sugar and the surrounding air at the freshly formed surface.

To test the latter hypothesis, the spark has been produced by dropping a lump of sugar in a tall receiver, and it was found that the colour and intensity of the flash were independent of the pressure of the air—between 76 c.m. and 2 c.m. And likewise when coal-gas was substituted for air it was also found that wetting the surface of the sugar did not alter the effect; and when two lumps of sugar were struck in water, the interesting result was obtained that the light was—so far as could be judged by merely looking at it—precisely similar to that obtained in air and coal-gas.

The fact that the surrounding medium does not seem to affect either the colour or intensity of the luminosity suggests that the effect is not due to any influence of a chemical nature of the surrounding medium on the sugar, but favours the former hypothesis that the luminosity is due to the peculiar structure of the sugar itself. The experiments are being pursued further.

NEW LABORATORY GAS FURNACE.

Our illustrations show a new fireclay gas furnace manufactured by Messrs. J. J. Griffin and Sons, on lines suggested by Mr. G. T. Holloway, for use by assayers, &c., or for performing any of the furnace work required in a chemical laboratory.

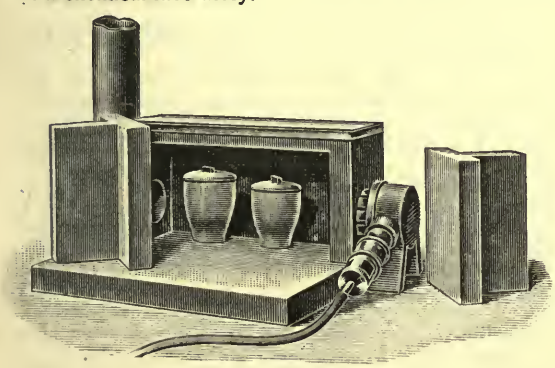


Fig. 1.

From the first illustration it will be seen that the furnace base extends forward beyond the body, and forms a convenient stand for hot crucibles, &c., and for the doors when they are drawn forward. The deep flanges on the doors serve as handles for moving them when the

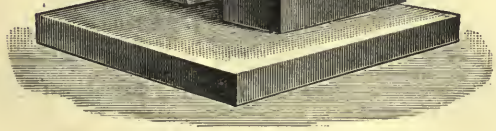


Fig. 2.

furnace is in use, and also support them in position and render them reversible.

The base and body are made in independent parts, so that either may be replaced at small cost, and the base may reversed when spoiled on one side by slags, &c. This independence of body and base renders it possible to produce the furnace at a lower cost than usual and facilitates packing and transport, and it has the further advantage that the cracking which takes place with all internally-fired fire-clay furnaces is less than in those made in one piece.

For roasting, heating platinum and other small crucibles, cupelling, scorifying, and general muffle work an extra door is supplied, through which a muffle passes. The second figure shows this appliance, the body of the furnace having been removed from the base to show the arrangement more clearly, and the small door which closes the muffle aperture being shown drawn aside. The back of the muffle rests on a removable block, as shown.

This furnace, which is about 13 inches in length, is found to be suitable for all the ordinary work of a laboratory, the various improvements in its construction also greatly facilitating the work done with it.

THE PREPARATION AND PROPERTIES OF HYDRIDE OF CALCIUM.

By HENRI MOISSAN.

Preparation.—Pure crystallised calcium, prepared by the method we described in a previous communication (*Comptes Rendus*, cxxvi., p. 1753, June 20, 1898) is put into a nickel boat in a glass tube traversed by a current of pure dry hydrogen. The hydrogen is purified by being passed through two porcelain tubes at a red heat,—one filled with copper and the other with pure boron. It is then dried with fused potash and phosphoric acid, previously calcined in a current of oxygen.

At the ordinary temperature calcium does not react on hydrogen.

When the tube containing the nickel boat has been well swept by a rapid current of hydrogen, the end of the tube is sealed and the hydrogen is kept in it at a pressure of from 30 to 40 c.m. of water. The temperature of the boat containing the lime is then slowly raised, and when it reaches a dull red heat we can see it take fire in the atmosphere of hydrogen. The gas is absorbed with great rapidity, and we obtain, in place of the metal, a white substance, which is hydride of calcium.

If we perform this experiment on 1 or 2 grms. of calcium it may be done in a glass tube, but the great disengagement of heat produced by this combination may give rise to the reduction of the glass by the alkaline earthy metal, producing black spots on the glass by the setting free of small quantities of silicon.

When the reaction is carried out in nickel boats, as we have already described, it is advisable not to work on more than 5 or 6 grms. of material at a time, or else the temperature becomes too high, and we more frequently find a crystallised alloy of nickel and calcium at the line of contact with the metallic nickel.

When we wish to get a higher return of this hydride we can easily do so by putting several boats containing calcium in the tube, so that the reaction will be performed successively. The metallic tube is then placed on a gas furnace with eight jets, and by using three boats we can easily work with 15 grms. of calcium.

If the hydrogen contains nitrogen, we notice that the hydride takes a greyish yellow tint and gives off ammonia by its decomposition with water.

Properties.—Hydride of calcium is a white body, and after fusion has a crystalline fracture. Examined under the microscope it appears in thin transparent layers, some of which are again covered by very small crystals. It does not perceptibly dissociate up to a temperature of 600° *in vacuo*. Its density taken in essence of turpentine is 1·7.

In hydrogen gas we have kept hydride of calcium intact up to a temperature of the melting-point of Bohemian glass; there was neither any absorption of gas nor apparent decomposition of the hydride.

In a current of chlorine, hydride of calcium does not change to any perceptible extent in the cold; but as soon as the temperature is slightly raised, long before any sign of redness, it burns with a flame, certainly not very bright, but giving off fumes rich in hydrochloric acid. After this reaction there remains a mass having all the properties of chloride of calcium, but not containing any sub-chloride. When heated in the vapour of bromine at a dull red heat the reaction is much stronger, and the hydride decomposes with a brilliant incandescence. This same reaction occurs with iodine; a brilliant light is suddenly produced at a red heat, and at the same time there is a production of hydriodic gas.

When heated on a sheet of platinum in free air, hydride of calcium undergoes no apparent change, even at a red heat, but if heated before an oxy-hydrogen blowpipe it burns with great brilliancy, producing at the same time a flame of hydrogen. After this experiment there remains only quicklime which has been raised to its melting-point. This residue treated with water forms at first a hydrate of lime, which disintegrates forming a greyish powder, which on further treatment with water gives off hydrogen. In this strong combustion of hydride of calcium in air, a layer of lime is formed, which—on account of the heat given off by the reaction—melts, and thus covers a part of the hydride and prevents complete oxidation. When thrown into the flame of a Bunsen burner, powdered hydride of calcium gives brilliant sparks, as does lime.

In a current of pure oxygen the hydride takes fire below a red heat, and continues to burn with strong incandescence. The heat given off is so great that one can distinctly observe the fusion of the lime produced. Examined under the microscope this lime appears to be covered with small crystals. We have already shown, by our experiments with the electric furnace, with what facility lime crystallises at a high temperature.

Hydride of calcium, either in powder or in small lumps, when heated in the vapour of sulphur to a dull red heat, forms only a small quantity of sulphide, the decomposition not being complete. But if we heat a fragment of the hydride in front of the blowpipe, the reaction takes place immediately with brilliant incandescence; at the same time an abundance of sulphuretted hydrogen is given off.

At the temperature of the melting-point of glass, hydride of calcium does not react on the vapour of selenium. When heated under a glass cover filled with nitrogen, hydride of calcium undergoes no change, even when the experiment lasts two hours. After cooling the volume of gas has not altered, and a sensitive litmus-paper gives no appreciable indication of ammonia. Thus, at a dull red heat nitrogen is without action on this hydride.

On the other hand, hydride of calcium is decomposed by the vapour of phosphorus at about 500°. Hydrogen is given off, and a substance of a deep chocolate colour remains, which reacts with cold water, giving phosphuretted hydrogen.

At a temperature of 700° boron has no action on hydride of calcium. When heated to from 700° to 800° in a crucible brasqued with previously baked charcoal, hydride of calcium is partially decomposed, and carbide of calcium, giving acetylene gas on contact with water, is formed. Under similar conditions silicon and boron gave no results.

Fluoride of potassium, first melted and then powdered, was mixed with powdered hydride of calcium; this mixture heated in a test-tube gave no active result until a temperature of 500° was reached, when the hydride reacted and gave off hydrogen and vapour of potassium. Fluoride of sodium gave the same reaction.

Fluoride of silver, when ground in the cold with this hydride, became incandescent, and deflagration was produced by the admixture of powdered fluoride of calcium and metallic silver. The fluorides of lead and zinc are reduced with incandescence below 400°.

Chloride of sodium, reduced to a fine powder and mixed with hydride of calcium, undergoes at a red heat a regular decomposition, giving off vapour of sodium, which condenses, forming a metallic mirror on the cooler part of the apparatus.

Melted iodide of potassium is not attacked by hydride of calcium, while iodide of silver, when warmed, reacts with a considerable disengagement of heat.

Oxidising agents, such as chlorate or bichromate of potassium when melted, or powdered permanganate of potassium, are reduced with incandescence. The chlorates, bromates, and iodates form veritable explosives with this hydride. With perchlorate of potassium the explosion takes place in the cold, by the simple grinding of the two substances in an agate mortar. If a few m.grms. of the hydride are mixed with an excess of perchlorate of potassium, the explosion is sufficiently violent to smash the tube to pieces.

Sulphuretted hydrogen does not react below a red heat, but at a higher temperature sulphide of calcium and hydrogen are formed.

If we heat powdered hydride of calcium in an atmosphere of binoxide of nitrogen, before a red heat is reached, a lively incandescence is produced and ammonia is given off very freely.

Carbonic acid is reduced at a red heat by hydride of calcium, with strong incandescence, carbon and carbide of calcium being formed.

Warm concentrated sulphuric acid is reduced by hydride of calcium.

Fuming nitric acid has practically no action. On the other hand, these same acids when diluted with water have a vigorous action; a salt of lime is produced, and hydrogen is given off. Concentrated or dilute hydrochloric acid attacks hydride of calcium. This reaction is comparable with that which gives us hydride of copper. Anhydrous ethylic alcohol attacks it but slowly, and both benzine and essence of turpentine, when quite free from water, have no reaction in the cold. The alcoholic chlorides and iodides are without action at the ordinary temperature. The vapour of tetrachloride of carbon is decomposed by this hydride with incandescence, at about 400°, with the production of a deposit of carbon and a disengagement of hydrogen and hydrochloric acid.

The most curious reaction of this new compound is that which takes place with cold water; as soon as hydride of calcium comes in contact with this liquid, the latter is decomposed with violence, and both the hydrogen of the water as well as that from the hydride is given off, while hydrated oxide of calcium is formed:—

$$CaH_2 + 2H_2O = Ca(OH)_2 + H_6.$$

Analysis.—To determine the composition of the hydride of calcium, we made the following experiment:—A given weight of pure crystallised calcium is placed in a small tared glass tube full of hydrogen. The exact weight of the metal is taken, and then it is transformed into hydride.

Weight of calcium	0·3595 grms.
Weight of hydride	0·3760 „
Hydrogen absorbed ..	0·0165 „

which corresponds to the following centesimal composition:—

		Theory for CaH_2.
Calcium	95·61	95·23
Hydrogen	4·39	4·76

The 0·376 grm. of hydride of calcium is placed in a large gas measurer filled with mercury; into the upper part of the apparatus a few c.c. of water are passed, which immediately decompose the hydride giving a volume of

hydrogen of 437 c.c. (H=766 m.m. T=+20°). The purity of this hydrogen was established by a eudiometric analysis. This volume, corrected to 0° and 760 m.m. =401·00 c.c. Theoretically, if we give to hydride of calcium the formula CaH_2 it should have produced a volume of 399·80 c.c.

Two other analyses, made under the same conditions, gave us the following figures:—

	I.	II.
Calcium	95·80	95·38
Hydrogen ..	4·32	4·60

Conclusions.—To sum up, we obtain by the direct union of calcium and of hydrogen, a transparent crystalline hydride, with the formula CaH_2. The hydride is stable at a high temperature, and is an energetic reducing agent. By its violent decomposition when in contact with cold water it strongly resembles the definite crystallised carbide of calcium we prepared in the electric. In this compound the hydrogen is comparable to the metalloids (carbon or phosphorus) and not to the metals. Even the appearance of this hydride completely distinguishes it from the hydrides of MM. Troost and Hautefeuille and the hydrogenised palladium of Graham. In reality there are two series of hydrides, some in which the hydrogen seems to be in solution in the metals, and the others forming at a more or less elevated temperature and presenting all the characteristics of definite chemical compounds.—*Comptes Rendus*, vol. cxxvii., No. 1.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Continued from p. 145).

Chlorine.

To make sure of getting all the chlorine, it is best to fuse with chlorine-free sodium-potassium carbonate, or even sodium carbonate alone, first over the full burner, then for a moment or two over the blast, leach with water, acidify with nitric acid, and precipitate by silver nitrate. If 1 grm. of material has been used no precipitation of silica need be feared on acidifying or on standing.

In many cases it is quite sufficient to attack the powder by hydrofluoric acid and a little nitric acid, with occasional stirring, and, after filtering through a large platinum cone, to throw down the chlorine by silver nitrate. The presence of nitric acid is necessary, since otherwise ferrous fluoride reduces silver nitrate with deposition of crystallised silver. When coagulated by heating and stirring, the precipitate is collected on the platinum cone, washed, dissolved by a little ammonia, and re-precipitated by nitric acid, when it can be collected in a Gooch crucible and weighed, or, if very small in quantity, on a small paper filter, which is then dried, wound up in a tared platinum wire, and carefully ignited. The increased weight of the wire is due to the metallic silver of the chloride which has alloyed with it.

Fluorine.

Fluorine can only be estimated by the method of Rose, care being taken to use sodium-potassium carbonate as a flux, and to avoid use of the blast if possible. The use of ammonium nitrate or chloride instead of carbonate for throwing out the silica and alumina is not to be recommended, because of loss of fluorine on evaporation (Rose). If the rocks are very basic, it may happen that the amount of silica in the alkaline solution is so small that ammonium carbonate may be dispensed with and the ammoniacal zinc oxide solution added at once.

By whatever modification of the method the silica may have been separated, the alkaline carbonate must be converted into nitrate and not chloride if phosphorus or chromium, or both, are present. To remove the chromium and the last of the phosphorus, silver nitrate in excess is added to the solution containing still enough alkaline carbonate to cause a copious precipitate of silver carbonate, in order to take up the acid set free, and thus ensure a neutral solution and consequent complete precipitation of phosphorus and chromium. After heating and filtering, the excess of silver is to be removed by sodium or potassium chloride, and sodium carbonate is to be added, when the fluorine is ready to be thrown out by calcium chloride in excess. At this stage there must be no ammoniacal salts in solution, otherwise calcium fluoride may be held in solution.

The well-washed and gently ignited calcium fluoride finally obtained in the course of this method should be converted to sulphate as a check upon its purity, and at the same time as a qualitative test to ascertain if it really is calcium fluoride by the characteristic odour of its gas. Should fluorine be found, and the weight of sulphate not correspond to that of the fluoride, the former should be dissolved in hot nitric acid and tested for phosphorus by ammonium molybdate solution. If phosphate is absent the impurity may have been silica or calcium silicate—which of these it would be difficult to decide. In the former case the fluorine might be safely deduced from that of the sulphate, but not in the latter. If the rock were rich in sulphur it might happen that calcium sulphate would be thrown down with the fluoride, but this should be removed by thorough washing. If not, and it were certainly the only impurity present, the fluorine could be calculated, after conversion of the fluoride into sulphate, by the formula—

$$CaSO_4 - CaF_2 : 2F :: \text{diff. between impure } CaSO_4 \text{ and } CaF_2 : x.$$

It is an exceptional case when there is exact agreement between the weight of fluoride and sulphate, and with the small amounts usually met in rocks the error may be an appreciable one in percentage of fluorine, though of no great significance otherwise.

There is no qualitative test which will reveal with certainty the presence of fluorine in rocks. Heating the powder before the blowpipe with sodium metaphosphate on a piece of curved platinum foil inserted into one end of a glass tube, or in a bulb tube, is not to be relied on in all cases. While as little as one-tenth of 1 per cent of fluorine can sometimes be thus detected with ease, much larger amounts in another class of rocks may fail to show.

(To be continued).

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

NOTICES OF BOOKS.

The Extra Pharmacopœia. Revised in accordance with the "British Pharmacopœia," 1898. By WILLIAM MARTINDALE, F.L.S., F.C.S. Serotherapy, Organotherapy, Medical References, and a Therapeutic Index, by W. WYNNE WESTCOTT, M.B. (Lond.). Ninth Edition. London: H. K. Lewis. 1898. Pp. 686.

IT is about three years since the last edition of this valuable little work was published. Naturally there are many changes and additions to be found in this, the ninth edition. Medical and chemical science never stands still, but marches steadily onwards. Notwithstanding this fact, conservative views prevailed in the revision of "The British Pharmacopœia," but the newer unofficial remedies will be found in the volume now before us, with numerous details and references as to their use. There is a small list of errata which should not be overlooked, but taking it altogether the author is certainly to be congratulated in bringing out the present edition of a book so useful

to doctors and pharmaceutical chemists, and thus indirectly to the public at large.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Anorganische Chemie,
Vol. xv.

Supersaturation: its Dependence on Crystalline Form.—M. Nicol.—The author endeavours to prove the law that when, under certain conditions of experiment, two allotropic modifications of the substance dissolved or melted may exist, the phenomenon of supersaturation or of superfusion is possible. The word allotropic should here be taken in its widest meaning, including not only amorphous and crystalline forms of the same substance, but also the crystalline modifications which may result from the union of that substance with other free molecules, such as water of crystallisation. The author has experimented on many and various substances, among which are hyposulphite of soda, borax, acetate of lead, nitrates of potassium, ammonium, and silver, acetanilide, hydroquinone, acetamide, tartaric and nitric acids, &c.

On the Constitution of Inorganic Compounds.—A. Werner.—The compounds which are formed by Anderson's reaction form the subject-matter of this paper. This name is given to the transformation undergone by the chloroplatinates of a certain number of the organic bases by which they lose successively one and then two molecules of hydrochloric acid. The author shows that such compounds are formed on the model of the ammoniacal compounds of platinum.

On the Valence of Glucinum.—A. Rosenheim and P. Woge.—The authors support the bivalence of glucinum, because it forms with the binoxalates compounds whose preparation and properties they describe, and which are ordinary double salts, while under the same conditions the tri-valent metals give complex compounds which are not double salts. On the contrary, glucinum, like the bivalent metals, forms with the bi-tartrates complex compounds which are not double salts. The trivalent metals do not form the complex compounds. Glucina does not act in the same manner as Al_2O_3, Cr_2O_3, and Fe_2O_3 with the para-molybdates, but with solutions of the alkaline bisulphites it gives crystallised double salts, as do most of the bivalent metals. The molecular weight of chloride of glucinum, by the ebullition method, using pyridine as solvent, gives a number corresponding to the formula $GlCl_2$.

On the Compounds of Platinum and Tellurium.—M. Rœssler.—Certain crystallised compounds having the composition $PtTe_2$ and PtTe are described. The first was obtained by melting platinum with an excess of finely divided tellurium, then removing the excess of tellurium by means of a concentrated solution of potash. When melted under suitable conditions this compound loses an atom of tellurium, and on solidifying forms crystals consisting of PtTe. The author suspects, but has not yet proved, the existence of a third compound, Pt_2Te.

The Hydrates of Platino-cyanide of Magnesium and their Solubilities.—MM. Hellmuth, Baron Buxhœvden, and Tammrann.—If crystals of platinocyanide of magnesium are gradually heated in a saturated solution from 0° to 100° we note that the crystals change first from red to yellow, then to a bright greenish colour, and finally become white; these colourations correspond to four different hydrates, containing respectively 6·9 to 6·6 H_2O, 5 H_2O, 4 H_2O, and 2 H_2O. The conditions under which these phenomena occur are minutely described, and curves of solubilities have been made.

MISCELLANEOUS.

Charterhouse (William Rogers' Memorial) Science and Art Schools and Literary Institute.—The Winter Session of this, one of the largest Science and Art Schools of the United Kingdom, will commence on Saturday, September 24th. During the late Session upwards of 700 students, mostly elementary teachers, availed themselves of the privileges afforded by this Institute. Instruction of a decidedly practical character is given in most of the sciences at a nominal fee; whilst in Art, at an equally low rate, students may be advanced in their studies. Classes will be held to prepare candidates for Matriculation (Lond.), the Clerical, Medical (including Mental), Legal, and other Exams. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working in a well fitted laboratory. Aspirants for University Honours can, at a small expense, be assisted in their studies. Special opportunities for the study of Hygiene will be afforded this Session to Laundry and Cookery students who desire to be prepared for the examinations held by the London School Board and by the London County Council. Full particulars of the classes may be obtained from Mr. C. Smith. Those interested in education will rejoice to learn that the work commenced by the late Rev. William Rogers, M.A., and continued by a late Vice-Chairman of the London School Board, is so vigorously continued by the present President, the Rev. Henry Swann, M.A.

On the Essence of Mandarins.—J. Flatau and H. Labbé.—The authors have found 98 per cent of limonene in this essence, identical with that found in essence of Portugal, a trace of citral, and about 1 per cent of the same ether insoluble in alcohol were also present.—*Bull. Soc. Chim. de Paris.*

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THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2027.

ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION.

BRISTOL, 1898.

By Professor W. E. AYRTON, F.R.S.,
President of the Section.

(Concluded from p. 154).

COMING now to physics proper, there is one branch which, although of deep interest, has hitherto been much neglected. We possess three senses which enable us to detect the presence of things at a distance—viz., seeing, hearing, and smelling. The first two are highly cultivated in man, and, probably for that reason, the laws of the propagation of the disturbances which affect the eyes and the ears have been the subject of much investigation, whereas, although to many animals the sense of smell is of far greater importance than those of seeing or hearing, and although, even in the human brain, a whole segment—a small one in modern man, it is true—is devoted to the olfactory fibres, the laws of the production and propagation of smell have received practically no attention from the physicist. For some time past it has, therefore, seemed to me to be of theoretical and practical importance to examine more fully into the physics of smell. Various other occupations have hitherto prevented my advancing much beyond the threshold of the subject, but, as it seems to me to open up what is practically a new field of inquiry for the physicist, I take this opportunity of putting on record some facts that have been already elucidated.

Various odoriferous substances have been employed in the experiments, and for several of these I am indebted to Mr. W. J. Pope. Although the physicist has been allowing the mechanical side of the subject to lie dormant, the chemist, I find, has been analysing flowers and other bodies used in the manufacture of scents, and then synthetically preparing the odoriferous constituents. In this way, Mr. Pope informs me, there has been added to the list of manufactured articles, during the past seven years or so, vanilin, heliotropin, artificial musk, irone, and ionone, which give the perfume of the violet; citral, that of lemongrass; coumarin, that of hay, and various others; and specimens of several of these artificial scents, together with other strongly-smelling substances, he has kindly furnished me with.

If it be a proof of civilisation to retain but a remnant of a sense which is so keen in many types of dogs, then I may pride myself on having reached a very high state of civilisation. But with the present investigation in view, this pride has been of a very empty character, since I have been compelled to reject my own nose as quite lacking the sensitiveness that should characterise a philosophical measuring instrument. The ladies of my family, on the contrary, possess a nasal quickness which formerly seemed to me to be rather of the nature of a defect, since, at any rate in towns, there are so many more disagreeable odours than attractive ones. But on the present occasion their power of detecting slight smells, and the repugnance which they show in the case of so many of them, have stood me in good stead, and made it possible to put before you the following modest contribution to the subject.

There is a generally accepted idea that metals have smells, since if you take up a piece of metal at random or a coin out of your pocket, a smell can generally be detected. But I find that, as commercial aluminium, brass, bronze, copper, German-silver, gold, iron, silver, phosphor-bronze, steel, tin, and zinc are more and more carefully cleaned, they become more and more alike in emitting *no* smell, and, indeed, when they are *very clean* it seems impossible with the nose, even if it be a good one, to distinguish any one of these metals from the rest, or even to detect its presence. Brass, iron, and steel are the last to lose their characteristic odour with cleaning, and for some time I was not sure whether the last two could be rendered absolutely odourless, in consequence of the difficulty of placing them close to the nose without breathing on them, which, as explained later on, evolves the characteristic "copper" and "iron" smell. But experiment shows that, when very considerable care is taken both in the cleaning and the smelling, no odour can be detected even with iron or steel.

Contrary, then, to what is usually believed, metals appear to have no smell *per se*. Why, then, do several of them generally possess smells? The answer is simple; for I find that handling a piece of metal is one of the most efficient ways of causing it to acquire its characteristic smell, so that the mere fact of lifting up a piece of brass or iron to smell it may cause it to apparently acquire a metallic odour, even if it had none before. This experiment may be easily tried thus:—Clean a penny *very carefully* until all sense of odour is gone; then hold it in the hand for a few seconds, and it will smell—of copper, as we usually say. Leave it for a short time on a clean piece of paper, and it will be found that the metallic smell has entirely disappeared, or, at any rate, is not as strong as the smell of the paper on which it rests. The smell produced by the contact of the hand with the bronze will be marked if the closed hand containing it be only opened sufficiently for the nose to be inserted, and it can be still further increased by rubbing the coin between the fingers.

All the metals enumerated above, with the exception of gold and silver, can be made to produce a smell when thus treated, but the smells evolved by the various metals are quite different. Aluminium, tin, and zinc, I find, smell much the same when rubbed with the fingers, the odour, however, being quite different from that produced by brass, bronze, copper, German-silver, and phosphor-bronze, which all give the characteristic "copper" smell. Iron and steel give the strong "iron" smell, which, again, is quite different from that evolved by the other metals. In making these experiments it is important to carefully wash the hands after touching each metal to free them from the odour of that metal. It is also necessary to wait for a short time on each occasion after drying the hands, since it is not until they become again moist with perspiration that they are operative in bringing out the so-called smell of metals.

That the hands, when comparatively dry, do not bring out the smell of metals is in itself a disproof of the current idea that metals acquire a smell when slightly warmed. And this I have further tested by heating up specimens of all the above-mentioned metals to 120° Fahrenheit, in the sun, and finding that they acquire no smell when quite clean and untouched with the hands.

Again, dealing with the copper group, or with aluminium, *no* smell is produced by rubbing any one of them with dry table-salt, strong brine, or with wet salt, provided that a piece of linen is used as the rubber; but if the finger be substituted for the linen to rub on brine, a smell is observed with copper and German-silver, this smell, however, being rather like that of soda; and whether dry salt, brine, or wet salt be rubbed on aluminium, a smell is noticed if the finger be used as the rubber, this smell being very marked in the case of the brine or wet salt. Again, although even when linen soaked in brine, or having wet salt on it, is used to rub tin, iron, or steel, a faint smell is noticed; this is much increased when the finger is substituted for the piece of linen.

As a further illustration of the part played by the skin in causing metallic smells, it may be mentioned that the explanation of certain entirely contradictory results, which were obtained in the early part of the investigation, when linen soaked in strong brine was rubbed on aluminium, was ultimately traced to one layer of moist linen of the thickness of a pocket-handkerchief, allowing the finger to act through it, so that an odour was sometimes noticed on rubbing aluminium with the piece of linen soaked in brine. For it was found that when two or more layers of the same linen soaked in the same brine were employed to separate the finger from the aluminium during the rubbing, no smell could be detected.

From the preceding it seems that the smell in these cases is evolved partly by contact with the finger, partly by the action of the solution of salt, and partly by the rubbing of the solid particles of salt against the metals. That the friction of solid particles against metals is operative in evolving smells is also illustrated by the smell noticed when iron is filed, or when aluminium, iron, or steel is cleaned with glass-paper or emery-paper in the air. Indeed, the smell thus evolved by aluminium Mrs. Ayrton finds particularly offensive. A slight smell is also noticed if iron or steel be rubbed in the air with even a clean piece of dry linen, and each specimen of the copper group, with the exception of the phosphor-bronze, which was tried in this way, gave rise to a faint, rather agreeable smell. No indication of odour could, however, be thus produced with aluminium or zinc when both the metals and the linen rubber were quite clean. It should, however, be borne in mind that all these experiments, where very slight smells are noticed, and especially when the odour rapidly disappears on the cessation of the operation that produced it, are attended with a certain amount of doubt, for the linen rubber cannot be freed from the characteristic smell of "clean linen," no matter how carefully it may be washed.

Before, then, a metal can evolve a smell, chemical action must apparently take place, for rubbing the metal probably frees metallic particles, and facilitates the chemical action to which I shall refer. All chemical actions, however, in which metals take part do not produce smell; for example, no smell but that of soda, or of sugar, respectively, can be detected on rubbing any single one of the series of metals that I have enumerated with a lump of wet soda, or a lump of wet sugar, although chemical action certainly takes place. Again, no metallic smell is observable when dilute nitric acid is rubbed on copper, German-silver, phosphor-bronze, tin, or zinc, although the chemical action is very marked in the case of some of these metals. Weak vinegar or a weak solution of ammonia are also equally inoperative. On the other hand, merely breathing on brass, copper, iron, steel, or zinc, which has been rendered practically odourless by cleaning, produces a very distinct smell, while a very thin film of water placed on iron or steel evolves a still stronger odour. Such a film, however, produces but little effect with any of the metals except these two, and if the whole series is lightly touched in succession with the tongue, the iron and steel smell as strongly as when breathed on, the German-silver still more strongly than when breathed on or covered with a water film, and the other metals hardly at all.

Now, as regards the explanation of these metallic smells, which have hitherto been attributed to the metals themselves. This, I think, may be found in the odours produced when the metals are rubbed with linen soaked in dilute sulphuric acid. For here, apart from any contact of the metal with the skin, the aluminium, tin, and zinc are found to smell alike; the copper group also smell alike, and the iron and steel give rise to the characteristic "iron" smell, which, in this case, can be detected some feet away. Now, it is known that when hydrogen is evolved by the action of sulphuric acid on iron, the gas has a very unpleasant smell, and this, Dr. Tilden tells me, is due to the presence of hydrocarbons, and especially of paraffin. I have been, therefore, led to think that the smell of iron or steel when held in the hand is really due to the hydrocarbons to which this operation gives rise; and it is probable that no metallic particles, even in the form of vapour, reach the nose or even leave the metal. Hence, although smell may not, like sound, be propagated by vibration, it seems probable that particles of the metal with which we have been accustomed to associate the particular smell may no more come into contact with the olfactory nerves than a sounding musical instrument strikes against the drum of the ear.

And the same sort of result may occur when a metal is rubbed, for, although in that case particles may very likely be detached, it seems possible that the function of these metallic particles may be to act on the moisture of the air, and liberate hydrogen similarly contaminated; and that in this case also it is the impurities which produce the smell, and not the particles of the metal with which we have been accustomed to associate it.

This view I put forward tentatively, and to further elucidate the matter I am about to begin a series of smell tests in various gases, artificially dried, with metals as pure as can be obtained.

I next come to the diffusion of smell. From the experience we have of the considerable distance at which a good nose can detect a smell, and the quickness with which the opening of a bottle of scent, for example, can be detected at a distance, I imagined that tubes not less than 15 or 20 feet in length would be required for ascertaining, even roughly, the velocity at which a smell travels. But experiment soon showed that when the space through which a smell had to pass was screened from draughts, it diffused with surprising slowness, and that feet could be replaced by inches in deciding on the lengths of the tubes to be used. These are made of glass, which is relatively easy to free from remanent smells.

When the room and tube had been freed from smell by strong currents of air blown through them, the tube was corked up at one end and taken outside to have another cork, to which was attached some odoriferous substance, inserted at the other end. The tube was now brought back to the odourless room, and placed in a fixed horizontal or vertical position, and the unscented stopper was withdrawn. As a rule, immediately after the removal of the stopper, a smell was observed, which had been transmitted very quickly through the tube by the act of corking up the other end with the stopper carrying the odoriferous material. This first whiff, however, lasted only a very short time, and then a long period elapsed before any further smell could be detected at the free end of the tube, whether that end was left open or closed between times. Finally, however, after, for example, about eighteen minutes in the case of a 3-foot horizontal tube, having a large cotton-wool sponge saturated with oil of limes attached to one cork, the smell became definite and recognisable.

It would, therefore, appear that the passage of smell is generally far more due to the actual motion of the air containing it than to the diffusion of the odoriferous substance through the air. And, as a striking illustration of this, the following is interesting:—After the stopper had been in contact with the odoriferous substance for some time, it, of course, acquired a smell itself, which gradually spread in the room in which the experiment was made. And although this smell was due simply to the exposed part of the stopper, while the air inside the tube was at one end in contact with a mass of the odoriferous substance itself, the only place where the smell could *not* be detected during the course of the experiment was the space inside the open end of the glass tube. And, what seemed very surprising, it was found necessary, in several cases, to blow air through the room to clear out the smell which emanated from the *outside* of the stopper before the smell coming along the tube from the mass of odoriferous

substance which was *inside* it at the other end could be detected. A further proof of the important part played by the motion of the air in diffusing smell was the fact that a strong smell at the free end of the tube could at any time be caused by merely loosening the stopper to which the scented sponge was attached; for sniffing at the free end then made a draught through the tube which brought the scent with it.

Further, although the glass tubes were coated outside with a thick layer of non-heat-conducting material, so as to check the formation of convection currents, due to difference in the inside and outside temperature, caused by handling, the rate of travel of a smell from a given odoriferous material was found to be much quicker when the tube was vertical than when it was horizontal. But this, I am inclined to think, may have been caused by a small convection current which still was produced in spite of these precautions.

For, as suggested by Dr. Ramsay several years ago, a substance must have a molecular weight at least fifteen times that of hydrogen to produce a sensation of smell at all, and, further, since camphor—with which many of my experiments have been made—has, when vaporised, a density about five times that of the air, it seems unlikely that scent vapour should diffuse much more quickly upwards through a vertical column of air than through a horizontal one. At the same time, not only are the tests with the glass tubes very striking, but the general impression which exists that smells rise,—indeed the very fact that the nasal channels of animals open downwards, tends to show that, whether due to draughts or not, smells have really a tendency to ascend. And the following result obtained with glass tubes closed at one end with stoppers carrying respectively camphor, menthol, oil of limes, &c., and at the other end with corks, is instructive on this point. For, on uncorking such a tube after it had been closed for a long time and allowing the odour to stream out of it through the open air towards the experimenter's face, it was always found that the tube had to be brought much closer when the scent stream was poured downwards than when she was in a vertical position and it was allowed to ascend, although, when it was poured downwards, the experimenter brought her nose into as favourable a position as possible for receiving the smell, by lying down with her head thrown well back.

As an illustration of the inefficiency of diffusion alone to convey a smell, you will find that if you hold your breath, without in any way closing your nose either externally or by contracting the nasal muscles, you will experience no smelling sensation even when the nose is held close to pepper or a strong solution of ammonia, or even when camphor on a minute tube is introduced high up into the nostril. Mere diffusion from the lower nasal cavity into the upper cannot apparently take place with sufficient ease to produce the sense of smell, so that an actual stream of air through the upper portion of the nose seems necessary even when the nose is a very sensitive one. This stream, for substances placed outside the nose, is produced by breathing *in*, no smell being detected while breathing *out*. On the other hand, if a substance be placed inside the mouth its flavour is recognised when the air is forced outwards through the nostrils—that is, at each expiration. Hence we may experience alternately two totally different smells by placing one substance outside the nose and the other in the mouth, the one smell being noticed in inhaling and the other in exhaling. And the latter can be increased by smacking the lips, which, I think, has really for its object the forcing of more air through the nostrils at each expiration.

Experiments on the propagation of smells in a vacuum have also been commenced in my laboratory, and the results are no less surprising than those obtained with the propagation in air. A U-tube, 7 inches high, had the odoriferous substance placed inside it at the top of one limb, and a very good vacuum could be made by allowing mercury to flow out of the tube. Then the two limbs were separated by raising the mercury column, and air being admitted at the top of the other limb, without its coming into contact with the odoriferous substance, the nose was applied at the top of this limb.

When liquids like ammoniated lavender, smelling salts, solution of musk, and amyl acetate were employed, and various devices were used for introducing the liquid, and preventing its splashing when it boiled on exhausting the air, it was found that the time that it was necessary to leave the two limbs connected for a smell to be just observable was reduced from a few minutes or seconds when the tube was filled with air to less than half a second for a good vacuum; with solid camphor it was reduced from twenty minutes to one second, and when moist rose leaves were used from fifty minutes to two seconds. But with solid particles of musk the time was not reduced below twenty minutes by taking away the air, while with dried lavender flowers and dried woodruff leaves no smell could be detected after the two limbs had been connected for many hours, and a good vacuum maintained, These experiments are, of course, somewhat complicated by variations in the amount of odorous surface exposed, but they seem to indicate that with these particular dried substances either the rate of evolution of the seent or its rate of propagation, or both, are very slow even in a good vacuum.

I have also carried out some tests on the power of different substances to absorb various scents from the air. Lard, it is well known, is used to absorb the perfume from flowers in the commercial manufacture of scents, perhaps because it has little odour of its own, and because the scent can be easily distilled from it. But if lard, wool, linen, blotting-paper, silk, &c., be shut up for some hours in a box at equal distances from jasmine flowers, dried woodruff leaves, or from a solution of ammonia, I find that it is not the lard, but the blotting-paper, that smells most strongly when the articles are removed from the box. On the other hand, when solid natural musk is employed, it is the wool that alone acquires much smell, even after the box has been shut up for days.

Another noteworthy fact is the comparatively rapid rate at which grains of natural musk are found to lose their fragrance when exposed to the air. The popular statement, therefore, that a grain of musk will scent a room for years supplies but another example of the contrast between text-book information and laboratory experience.

The power of a smell to cling to a substance seems to depend neither on the intensity of the smell nor on the ease with which it travels through a closed space. Musk has but a faint smell, but the recollection of the greeting of a rich Oriental survives many washings of the hands. The smell of rose leaves, again, is but faint, and it travels very slowly through air in a tube; and yet the experiments on its propagation in the glass vacuum apparatus were rendered extremely troublesome, by the difficulty experienced in removing the traces of the smell from the glass between the successive tests. Rubbing its surface was quite ineffectual, and even the mercury had to be occasionally shaken up with alcohol to free it from the remanent smell. In fact we found, as Moore put it,—

> "You may break, you may shatter the vase if you will,
> But the scent of the roses will cling to it still."

This absorption of scents by glass, and the ease with which I found that jasmine flowers could be distinguished from woodruff leaves, even when each was enclosed in a series of three envelopes specially prepared from glazed paper, and when many precautions were taken to prevent an odour being given to any of the envelopes in the operation of closing, as well as to prevent its diffusion through the joins in the paper, led me to try whether an actual transpiration through glass could be detected with the nose. For this object a number of extremely thin glass bulbs were blown from soda and from lead glass, so thin that they exhibited colours like a soap-bubble, and felt, when gently touched, like very thin oiled silk; and

after a little ammoniated lavender, amyl nitrite, ethyl sulphide, mercaptan, solution of musk, oil of peppermint, and propylamine had been introduced into them respectively, they were hermetically sealed, and placed separately in glass stoppered bottles.

In some cases, on removing the stopper from a bottle after many hours, a faint odour could be detected, but so, generally, could a minute flaw after much searching; the crack, however, being so slight that it did not allow sufficient passage of the air to prevent the bulb subsequently breaking, presumably from changes of atmospheric pressure. And in those cases where a smell was detected without any flaw being found in the glass, the subsequent breaking of the bulb put an end to further testing. The question, therefore, remains unanswered.

In presenting this brief introduction to the physics of smell, I have aimed at indicating the vast territory that waits to be explored. That it will be found to contain mines of theoretical wealth there can be no doubt; while it is probable that a luxuriant growth of technical application would spring up later on. Already, for example, Mrs. Ayrton unintentionally picks out inferior glass by the repugnance she shows at drinking water out of certain cheap tumblers. To conclude, I may say that one of my fondest hopes is that an inquiry into the physics of smell may add another to the list of wide regions of knowledge opened up by the theoretical physicist in his search for answers to the questions of the technical man.

ON THE COOLING CURVES OF FATTY ACIDS.*

By A. P. LAURIE and E. H. STRANGE.

THE melting-points of mixtures of fatty acids were determined by Heintz, and the tables are quoted in the text-books. They show that the mixtures have a lower melting-point than either of their constituents, thus showing a close analogy to the behaviour of many alloys. We therefore determined to apply to these bodies a method of investigation similar to that used by Professor Roberts-Austen in his experiments on alloys.

The melted fatty acids are placed in a test-tube surrounded by melting ice, and a thermal junction connected to a mirror galvanometer inserted. The results are photographed on a moving plate. The plate is calibrated by means of a second thermal junction attached to a thermometer, and immersed in a large volume of water. The cooling curves obtained in this way are of considerable interest. The fatty acids investigated have been palmitic, stearic, lauric, and myristic acids. The cooling curve of a pure fatty acid turns sharply round when the solidifying point is reached, runs straight up the plate till the solidifying is finished, and then turns sharply off again. One per cent of another fatty acid quite perceptibly alters the shape of the curve, so that the character of a cooling curve seems a good test of purity. When a larger portion of a fatty acid is introduced a second latent heat-point is developed, the curve showing a discontinuity below the solidifying point of the mixture. As the solidifying point is lowered by introducing more and more of the second fatty acid, this discontinuity is gradually merged in the common melting-point of the mixture, thus reproducing the phenomena observed by Professor Roberts-Austen in the case of certain alloys. The question, therefore, of the true cause of this discontinuity is opened up, as we can hardly suppose that two homologous acids are forming compounds. We are now repeating our experiments with synthetically prepared organic bodies of known constitution, and studying also the cooling curve of water.

* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

THE

CARBOHYDRATES OF THE CEREAL STRAWS.*

THE work, which was carried out in the agricultural season of 1897, has been reported upon in a paper published in the *Journal of the Chemical Society*, 1898, p. 459. The purpose of these later investigations was to trace the effect of removing the seed-bearing organs upon the carbohydrates of the stem. The results were, however, negative, adding another confirmation to the conclusion previously arrived at, that the carbohydrates of the stem tissues are built up with a constant ratio of "furfural-yielding" to normal hexose carbohydrates. Further evidence was also obtained that these two groups of carbohydrates are in the earlier stages of growth similarly attacked by boiling dilute acids, and after such hydrolysis are similarly fermented by yeast.

It must in fact be admitted that as condensation to furfural is by no means an exclusive characteristic of C_5 carbohydrates, there is no evidence whatever that the furfuroids of the barley straw are, in the early stages of growth, pentose-anhydrides or pentosanes.

There now appears in the *Journ. Fed. Inst. Brewing*, 1898, p. 438, an article by Tollens under the title "On the Carbohydrates of Barley and Malt, with special reference to the Pentosanes," in which, as a result of yeast fermentations of the products of acid hydrolysis of brewers' grains, the author arrives at the following conclusions:—"From the behaviour of these furfural-yielding substances on fermentation we are forced to the view that they behave, to some extent, similarly to the ordinary hexoses, and somewhat different from the pentoses, for when brought into contact with yeast they exhibit certain manifestations of fermentation; but they give rise to the formation of but little alcohol and much acid. It must be concluded from this that the furfural-yielding substances . . . contain a certain amount of other substances more susceptible to fermentation than arabinose and xylose. They may contain glycuronic acid or oxycelluloses. . . ."

We are very glad to have this confirmation from so great an authority as Professor Tollens, and we will not quarrel with his decision "to retain the old name pentosanes for this group of substances," instead of "the indefinite name of furfuroids proposed by Cross and Bevan." We will only remark that, as the idea has been abandoned that they are exclusively and definitely pentosanes, it appears more logical to adopt a term of corresponding significance.

We ourselves have recently carried out a more extended series of fermentation experiments which further define these products, and the results of this work will be published in the course of the autumn.

Generally, the position for which we have long contended may be taken as fully established, viz., that the plant world affords a group of furfural-yielding bodies, probably carbohydrates, which are susceptible of fermentation by yeast.

We have next resumed the study of the problem of the relationship of such compounds to the normal hexoses, on the basis of the purely chemical probabilities. We have previously shown that furfuroids are produced from the hexoses by many processes of oxidation. One such process, which we had overlooked, appeared from the researches of Fenton in the province of the dicarboxylic acids to be capable of extension to other hydroxy-compounds, such as the carbohydrates—that is, the action of hydrogen peroxide in presence of iron salts. A research in this direction has led to positive results. We have not only succeeded in producing furfuroids in some quantity—7 to 9 per cent of the hexaldoses—but we find that di-

* Third Report of the Committee, consisting of Professor R. Warington (Chairman), Mr. Manning Prentice, and Mr. C. F. Cross (Secretary). (Drawn up by Mr. Cross). Read before the British Association (Section B), Bristol Meeting, 1898.

carbonyl derivatives are produced reacting with phenylhydrazin acetate in the cold to form dihydrazones, which appear to be osazones. We have published a preliminary account of this research in the *Journal of the Chemical Society*, 1898, p. 463, and since the publication of the paper we have been joined in the investigations by Dr. R. S. Morrell, of Cambridge University. Results have been obtained confirming and extending those of our preliminary paper, and these will be published in the course of the autumn. We have every expectation that the investigations will lead to results of physiological significance by elucidating processes actually taking place in the plant cell.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E., *Water Examiner, Metropolis Water Act*, 1871.

London, September 10th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Aug. 1st to Aug. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us all were clear, bright, and well filtered.

The deficiency of rain still continues. The fall at Oxford during this month has been 1·64 inches; this fell on eight days. The average for the last thirty years is 2·32 inches, leaving a deficiency of 0·68 inch. The total deficiency for the year is now 6·17 inches, or 38 per cent.

Our bacteriological examinations of 255 samples have given the results recorded in the following table; we have also examined 36 other samples, from special wells, standpipes, &c., making a total of 291 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	690
New River, filtered (mean of 25 samples) ..	70
Thames, unfiltered (mean of 26 samples) ..	2620
Thames water, from the clear water wells of five Thames-derived supplies (mean of 126 samples)	28
Ditto ditto .. .. highest	493
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	1958
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	51

The excellent quality of the water supplied to London during the past month has been thoroughly maintained.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

A NEW DEPARTURE IN THE MANUFACTURE OF SALTS OF THE HIGHER OXIDES.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

UNFORTUNATELY, so far, no satisfactory method for the manufacture of the above-mentioned compounds has been introduced, save that of fusion of the said oxide in contact with alkali bases. This method, besides being tedious, is at the same time most destructive upon the plant employed, which naturally accounts in a large measure for the still high market rate of these compounds.

True, a partial improvement in the method of fusion was introduced by the author some years previously, by the introduction of suitable quantities of alkaline borates in proportion to the melt. This, besides effecting a more complete union at a much lower temperature, also effects a considerable saving of the plant in use; whilst, at the same time, the lowering of the temperature naturally prevents to a large extent volatilisation of the alkalis.

In order, therefore, to surmount as much as possible the former obstacles, several electrolytic processes have of late been protected, each differing from the other with a sufficiency to admit of the inventor securing a further protection only, either as regards electrolytes employed, or, on the other hand, the choice of suitable diaphragms has been discussed. Bearing these facts in mind, the author is about to establish a more direct process, which, with due precautions, it is hoped will evolve a more theoretical yield than any of the processes now in use.

A general and condensed outline of the new process is as follows:—It consists of the conversion of such alloys as spiegeleisen, ferromanganese, chromeisen, &c., by the direct contact of aqueous solutions of the alkalis aided by electric energy, into their corresponding salts, such as chromates, manganates, &c. The baths for the conversion of these alloys have so far been constructed of glass and partially covered with graphite plates, which constitute the negative electrolyte, while to the positive is attached the alloy in question. The solution or solvent employed, consisting for the most part of caustic alkali of a definite gravity to which has been added a small percentage of other oxidants which have been found to aid in the conversion, which takes place rapidly under a pressure of 8 volts, with the formation of manganates or permanganates, as desired (ferrates may, if desired, be thus obtained, or a corresponding oxide precipitated), or by slight alteration of the process a solution of chromate may be obtained.

Liverpool Research Laboratory,
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ON SELENITE OF COPPER AND ITS USE IN THE PREPARATION OF SELENIC ACID.

By R. METZNER.

I. *Preparation of Seleniate of Copper.*

SELENIUM was transformed into a solution of selenious acid; this was oxidised by means of a current of chlorine. The reaction which takes place is the following:—

$$SeO_2 + 2Cl + H_2O = 2HCl + SeO_3.$$

It is exothermic, and gives off about +30 cals.

It is as well not to operate on a too concentrated solution; the proportion present should not exceed 10 per cent, if we wish to get a complete oxidation. When the liquid has taken a yellow tint and gives off a strong odour of chlorine, we prove on a small sample that there is no more selenious acid present. We then proceed with the neutralisation of the mixture of the selenic and hydrochloric acids by means of pure oxide of copper made by the calcination of the nitrate; this dissolves rapidly,

giving a solution at first green, but becoming blue when the neutralisation is almost complete. We then add oxide of copper precipitated from the nitrate and perfectly washed with warm water, and which is further boiled to diminish its volume. This oxide dissolves much more rapidly than the calcined oxide, and by its use we can easily neutralise the selenic acid. The solution obtained, mixed with chloride and seleniate of copper, is partially evaporated down; on cooling it deposits beautiful prisms of seleniate of copper, which are carefully dried, and purified by further crystallisations effected by allowing the hot saturated solutions to cool; this salt is, as we shall see later on, much more soluble hot than cold. Further, chloride of copper being deliquescent, the concentration of the mixture of the seleniate and the chloride can be pushed very far, and, the former being insoluble in a saturated solution of the latter, we obtain a complete separation.

The chlorine I used was from an iron reservoir containing the gas in the liquid state; thus I experienced no difficulty in preparing several kilogrms. of seleniate of copper.

It is certain that it would be more easy to effect the operation of the selenious acid with bromine, and I tried the operation under the same conditions of dilution as with the chlorine. The reaction which might take place is the following one:—

$$SeO_2+2Br+H_2O=2HBr+SeO_3.$$

It also gives off 10·4 cals.; but the oxidation which is partially produced when we pour bromine water into a solution of selenious acid is never complete, and, if we add the theoretical quantity of bromine necessary to oxidise a determined quantity of selenious acid, the liquor remains coloured by bromine, while at the same time unoxidised selenious acid remains.

II. *Properties of Seleniate of Copper.*

Solubility.—This varies greatly with the temperature. I have found in 1 litre of a saturated solution:—

At 15°	257	grms. of seleniate.
At 35°	346	„ „
At 55°	435	„ „

At a higher temperature towards 70° a saturated solution of seleniate of copper decomposes, as has been shown by Mitscherlich (*Ann. de Chim. et de Phys.*, Series 2, vol. xxxvii.), depositing a green crystalline matter which he could not analyse, but which corresponds to the formula $2(CuOSeO_3),CuO,5H_2O$, as is shown by the following analysis:—

	Found. I.	Found. II.	Mean.	Calculated.
Copper ..	31·0	29·9	30·45	31·1
Selenium..	27·0	26·8	26·9	26·7

The deposit is the more abundant as the liquor contains more seleniate, so that in order to obtain a notable quantity it is necessary to commence with a solution saturated at 50°. Seen through the microscope this substance appears to consist of small clinorhombic prisms, transparent, pale green, and unmodified. They are but slightly affected by cold water, which enables them to be washed to get rid of the mother-liquor.

Selenide of copper dissolves, especially when warmed, in selenic acid, diluted with three or four times its volume of water. On cooling, the solution leaves a deposit of pale blue striated prisms, in which I have found copper 20·6, selenium 27·0, and which have therefore the same composition as the original crystals.

When the amount of selenic acid is augmented, the above blue crystals become transformed into a granular white matter, which under the microscope—even with a low power—appear to be formed of transparent tabular crystals. They correspond to the formula $CuO,SeO_3,2H_2O$. When submitted to the action of dry air, the crystals of seleniate of copper lose water. At 100° only one molecule remains, and the crystals then correspond to the formula CuO,SeO_3,H_2O.

Heat of Formation.—This has been measured by precipitating a normal solution of seleniate of copper by an equivalent quantity of potash in the calorimeter. I thus found—

$$SeO_4Cu+2KOH=SeO_4K_2+CuO \text{ ppt.}+H_2O= \\ =+13{\cdot}06 \text{ cals.},$$

from which it is deduced that—

SeO_3 dis. + CuO ppt. = SeO_4Cu dis. . . . + 18·12 cals

Heat of Solution.—We found for this—

$SeO_3,CuO,5H_2O$ + water = SeO_4Cu dis. . . . −2·66 cals.

III. *Electrolysis.*

Pure seleniate of copper was obtained, as has been described above, but more especially free from hydrochloric acid; I effected its electrolysis warm, by operating on saturated solutions.

The apparatus, which is very simple, is composed of two large platinum crucibles; one of them, the larger, was placed at the bottom of a very wide porcelain crucible holding the solution; the other, smaller one, was suspended a short distance from the first one by means of platinum wires. These two crucibles were connected with the poles of a dynamo, and the whole arranged so that the lower crucible should be entirely submerged, while the upper one was only partially so; by putting in mercury as ballast it could be made to sink to any desired distance from the lower one. Finally, a current of air kept the liquid thoroughly mixed so that the electrolysis was regular. With a current of two to three volts and five ampères the copper is deposited in the form of a light spongy mass, which falls into the lower crucible: in ten hours we obtained 300 c.c. of dilute monohydrated selenic acid, in 2 to 3 litres of water.

I have always carefully watched for the disappearance of the last traces of copper, so as not to keep the current on longer than the time necessary for complete separation, and to prevent the possible phenomena of reduction. I thus obtained a very pure selenic acid; I am especially certain that it contained neither copper, chlorine, nor selenious acid.—*Comptes Rendus*, cxxvii., No. 1.

ON THE ESTIMATION OF PHOSPHORIC ACID.

By H. LASNE.

In an article by Léo Vignon which recently appeared in the *Comptes Rendus* (vol. cxxvi., p. 1522), he pointed out the divergences obtained by the separate precipitation of the solutions of a superphosphate treated first with water, then with citrate of ammonia, or by previously mixing the two solutions. The total of the two first figures, he says, will always be less than the third, and that to a considerable degree. A result of this kind would be such as to throw doubt on the exactitude of the estimation of phosphoric acid by precipitation in presence of citrate of ammonia; while according to my experience I do not believe there is a more exact estimation, or one less subject to uncertainties, while at the same time it is thoroughly practicable. Every day in my laboratory we make a large number of estimations of phosphoric acid in superphosphates, often separating the results, and nothing of this kind has ever been observed.

We here give some experiments made since the publication of Léo Vignon's article, with a view to confirm in a special manner the observations we have just made.

I. Mineral superphosphate obtained from a phosphate from the Somme.
II. Superphosphate from degelatinised bones.
III. Superphosphate from green bones.

	Weight of pyrophosphate.		
	I.	II.	III.
	Grm.	Grm.	Grm.
On 1 grm. of superphosphate soluble in water	0·2622	0·1186	0·1320
Insoluble in water, but soluble in citrate	0·0089	0·1369	0·0400
Total	0·2711	0·2555	0·1720
On the two solutions united..	0·2715	0·2570	0·1732

The differences, it will be seen, hardly amount to a m.grm.,—that is to say, they come within the range of errors of observation; the experiments were purposely carried out under the same conditions as used in ordinary practice, and without any special precautions. The precipitations are always done in the evening, and the filtering takes place the following morning, after standing fifteen or sixteen hours. I have, however, shown (*Bull. Soc. Chim.*, Series 3, xvii., p. 823) that the precipitation is complete after three or four hours' standing or fifteen minutes' agitation, but that, under these conditions, there remains in the precipitate a small quantity of trimagnesic phosphate which disappears completely after sixteen hours' contact in presence of citrate of ammonia.

I have also shown (*loc. cit.*) that the precipitation is integral—that it is not influenced by substances which generally accompany phosphoric acid, except silica and fluorspar, which should be previously removed. But it fortunately happens that neither silica nor fluorspar enter into solutions with the superphosphates, otherwise the estimation would be complicated.

To sum up, the ammonio-magnesic phosphate is *completely* insoluble in a solution containing one-third of its volume of ammonia at 22°.

In order to confirm my previous results I made the following experiment with the greatest care, with the object of finding out whether very small quantities of phosphoric acid could be precipitated in the state of ammonio-magnesic phosphate:—

I. 3·5 grms. of phosphate of ammonia were dissolved in 100 c.c.
II. With 10 c.c. of No. I. I made 100 c.c.
III. With 10 c.c. of No. II. I made 100 c.c.
IV. With 10 c.c. of No. III. I made 100 c.c.

10 c.c. of each of these solutions were taken, and precipitated in the usual manner; that is to say:—
40 c.c. of water (to bring it up to the usual volume).
25 c.c. of citrate of ammonia at 400 grms. of citric acid per litre.
60 c.c. of ammonia at 22°.
20 c.c. of ammoniacal chloride of magnesia at 20 grms. of magnesia per litre.

If we add the wash waters of the precipitate we get a total volume of about 200 c.c. After calcining to form pyrophosphate I obtained the following weights:—

I.	II.	III.	IV.
0·3159	0·0317	0·0034	0·0003

That is in phosphoric acid:—

0·2121	0·0203	0·0021	0·0002

With an approximation which was entirely satisfactory I obtained down to the lowest figure the following proportion:—

1000 : 100 : 10 : 1.

I attach the greatest importance to Experiment No. IV. The beaker in which the precipitation took place, after having been emptied and drained, showed slight signs of losing its polish, caused by the crystals of the ammonio-magnesic phosphate. After weighing, the precipitate was re-dissolved, and the presence of phosphoric acid proved by means of nitro-molybdate of ammonium. From this it results that 1 m.grm. of phosphoric acid per litre is *integrally* precipitated in the state of ammonio-magnesic phosphate. There is therefore no reason to fear that the precipitation of very poor solutions is incomplete. If it does not immediately show in a distinct manner, it is sufficient to leave the solution, after agitation, from the evening to the next morning, for the whole of the phosphoric acid to be precipitated.

SOME PRINCIPLES AND METHODS OF ANALYSIS APPLIED TO SILICATE ROCKS.*

By W. F. HILLEBRAND.

(Concluded from p. 159).

Sulphur.

If present in the form of soluble sulphates, simple boiling with hydrochloric acid suffices, which should be done in an atmosphere of carbonic acid if pyrite or other oxidisable sulphides are present.

The sulphur of sulphides, chiefly pyritic, may sometimes be determined by extraction with aqua regia or potassium chlorate and hydrochloric acid, but not always; so that it is better by far to fuse with sulphur-free sodium carbonate and a little nitre over the Bunsen burner and for a few moments over the blast, fitting the crucible into a hole in asbestos board to prevent access of sulphur from the flame. The aqueous solution, after filtration, is just acidified by hydrochloric acid, and the sulphur at once thrown down at boiling heat by barium chloride, without fear of separation of silica in a bulk of about 250 c.c. when 1 grm. is operated on. It is well that this is so, for evaporation on the water-bath heated by gas to remove silica would in many cases involve an error fully equal to the sulphur present by contamination from the sulphur of the gas burned.

Owing to the small amount of sulphur in rocks, special purification of the barium sulphate obtained is hardly ever needful, especially as it has been precipitated in absence of iron. Should there be fear of a trace of silica being present, it can be removed by a drop of hydrofluoric and sulphuric acids before weighing the barium sulphate.

This, of course, gives the total sulphur in the rock. If soluble sulphates and sulphides as well as insoluble sulphates and sulphides are present together, the sulphur of the first is found in solution after extraction by hydrochloric acid in a carbon dioxide atmosphere, and that of the decomposable sulphides by collecting the hydrogen sulphide evolved. In the residue the sulphur of the insoluble sulphides can be estimated, or from the total sulphur found in another portion its amount can be calculated. The error involved in the above estimation of the sulphur of soluble sulphides, due to the possible reducing effect of hydrogen sulphide on ferric salts, is probably negligible. Most of the hydrogen sulphide would be expelled before any such action could take place and probably before the ferric salts were largely attacked, but of course the small proportion of sulphur set free as such from pyrrhotite would escape estimation and introduce further uncertainty. In general, it would be safe enough to assume the composition Fe_7S_8 for pyrrhotite. However carefully all these separate determinations may be carried out, the final figures for ferrous and ferric oxides can hardly be regarded as more than approximations when much sulphide is present.

Boron.

To the best of the writer's belief it has never been necessary in this laboratory to estimate boron in a silicate rock. Should it become necessary to do so, since most silico-borates are insoluble minerals, it would probably be necessary to fuse with sodium carbonate, extract with

* From the *Bulletin of the United States Geological Survey*, No. 148, p. 15, 1897.

water, and apply the method of Dr. Gooch (*Proc. Amer. Acad. Arts Sci.*, 1886, p. 167; *Bull. U.S. Geol. Survey*, No. 42, p. 64, 1887; CHEMICAL NEWS, vol. lv., p. 7, 1887), depending on expelling the boron as methyl borate by repeated distillations with methyl alcohol in nitric or acetic acid solutions, and binding the boric acid by a known weight of lime, the gain in weight being B_2O_3. Fluorine would have to be first removed by calcium nitrate or acetate before freeing the boron.

(For a useful improvement in the way of collecting the boric ether in ammonia before bringing in contact with the lime, &c., see Penfield and Sperry, *Am. Journ. Sci.*, 3rd Series, vol. xxxiv., p. 222, 1887; also Moissan, *Comptes Rendus*, vol. cxvi., p. 1087, 1893, and *Bull. Soc. Chimique*, vol. xii., p. 955, 1894, who modifies the Gooch distilling apparatus and insures complete condensation of the boron in the distillate).

Nitrogen.

Nitrogen has been found in igneous rocks, or the minerals occurring in them, by several observers. Thus, H. Rose ("Quantitative Analyse," Finkener edition, p. 673) says that pitchstone gives off ammoniacal water on heating; Silvestri (*Gazz. Chim. Ital.*, v., p. 303, 1875) mentions a nitride of iron in lavas from Etna; Sandberger finds ammonium carbonate to be given off from certain rocks of Pribram; the writer has shown nitrogen to exist in uraninite; Ramsay and others have noted it in traces with or without helium, &c., in numerous minerals; and lately Erdmann (*Ber. Deutsch. Chem. Gesell.*, xxix, p. 1710, 1896) has found it to be given off as ammonia on treating various minerals of "ancient igneous rocks" with a caustic alkali. Leudeking also found ammonium sulphate in a barite from Missouri, the presence of which the writer was able to confirm.

During the last two years it has been noted in this laboratory on three separate occasions, when analysing as many different series of ores, roofing-slates, and eruptive rocks, that ammonia, either in the form of chloride or sulphate or even as free ammonia, was given off on heating. Its appearance was not limited to one or a few specimens of a series, but seemed to be characteristic of all, and to be afforded by the unbroken rock as well as by the powdered sample. Not knowing the precise conditions under which the specimens were collected, it is impossible to affirm positively that the ammonia may not have been due to recent organic contamination of some sort, especially in the case of the slates, but it is believed that a more critical collection of material will not alter the general result. Its amount was sometimes readily determinable by Nesslerisation, being as high as 0·04 per cent in some slates. Carbonaceous organic matter was absent from most of these, but doubtless existed in them in their early history. In their case the ammonia was, in part at least, evolved as such, imparting a strong alkaline reaction to the water in the upper part of the tube. The presence of sulphides, fluorides, or chlorides in the rock might cause the ammonia to appear as a sublimate of sulphate, fluoride, or chloride. Speculation on this matter would be altogether premature, but attention is now called to it in the hope that other observers may be led to look for and investigate similar appearances. It should be borne in mind that the nitrogen present would not necessarily appear as ammonia or ammonium salts, since it might be given off in the elemental condition, as with the gases obtained from uraninite.

Special Operations.

The problem often presents itself of ascertaining the composition of that portion of a rock powder which is soluble in special reagents or in a reagent of a particular concentration. No precise directions can be formulated to meet such cases. The procedure must vary with the character of the constituents of the rock and with the object which it is sought to attain, and only in exceptional cases can a separation of this kind be sharp. Much depends on the degree of fineness of the powder and on the length of time it is exposed to the action of the reagent.

Detection of Nepheline in presence of Olivine.—For confirmation of the microscopic diagnosis, Prof. L. V. Pirsson (*Am. Journ. Sci.*, 4th Series, vol. ii., p. 142, 1896) has indicated a means of detecting nepheline in presence of olivine, as in nepheline basalts, based on the very ready solubility of nepheline, as compared with olivine, when boiled for but one minute with a sufficiency of very dilute nitric acid (1 : 40). Gelatinisation of the filtrate on evaporation is taken as evidence of the presence of nepheline. If olivine is present in quantity, however, this test must not be accepted at once as final, for some, if not all, olivines are much more soluble in nitric acid of the above strength than Professor Pirsson was led to believe from his original tests. If, therefore, on evaporation of the filtrate, much iron is indicated, the gelatinisation may well be due to olivine alone or in part, and then the quantitative relation of silica to iron plus magnesium should be ascertained. It must also be borne in mind that any other very soluble silicates present will be more or less affected, and that apatite is largely or wholly dissolved. It is possible that still more dilute nitric, or perhaps some other, acid may exert a slighter solvent action on olivine without being appreciably less effective in dissolving nepheline, &c. In combination with a quantitative analysis of the extract the method is, perhaps, susceptible of a wider application than the particular case for which it was first used. It is well worth further study.

Estimation of Soluble Silica.—Very often in treatment by acids silica is separated in gelatinous or granular form mixed with the unattacked minerals, and it becomes necessary to remove or estimate this silica, or else to discriminate between soluble and insoluble silica already existing together. Usually a boiling solution of sodium carbonate has been employed for this purpose. Its action is frequently slow and incomplete, and the extraction must often be repeated many times as to silica, and its solvent action on other minerals is often marked. The filtering of hot saturated solutions of the carbonate is also unpleasant. Hence the substitution of a caustic hydroxide, as KOH or NaOH, has been advocated, especially by Michaelis (*Chemiker Zeitung*, 1895, xix., p. 1422), who maintains with force that quartz is absolutely unattacked by boiling 10 per cent solutions (10 per cent Na_2O), or even by 25 per cent solutions when digested on the water-bath, and that different results are probably due to the mechanical carrying off in the filtrate of portions of the fine powder, which is notoriously difficult to filter. In the case of separated silica the hydroxides certainly give very good results. Solution is almost immediate and complete in a quite dilute liquid, and the difficulty met with in filtering may often be overcome by faintly acidifying. If the dilution is sufficient, no separation of silica results from so doing, and less difficulty is experienced in filtering and washing, especially if very dilute acid is used for the latter.

Estimation of Minute Traces of certain Constituents.

If, as sometimes may happen, the problem is presented of examining rocks for traces of gold, silver, and other elements which are not ordinarily looked for, as in Sandberger's investigations bearing on the origin of the metalliferous contents of veins, large weights of material must be taken, up to 50 grms. or more. This involves the use also of large quantities of reagents, the purity of which must then be looked to with the utmost care. Special directions to meet such cases cannot now be given, nor even a complete reference list of the scanty and scattered literature on this subject. Sandberger's own writings deal but little with its analytical side, and from its inaccessibility in the Washington libraries the writer is as yet unacquainted with the report by Von Foullon "Ueber den Gang und die Ausführung der Chemischen Untersuchung" ("Jahrbuch der Bergakademie, Leoben u. Pribram," 1887, p. 363), following Sandberger's own paper

in the general report "Untersuchungen der Nebengesteine der Pribramer Gänge" (see Note). The present writer has published a few data as to gold, silver, lead, zinc, &c. (*Mon. U.S. Geol. Survey*, vol. xii., 1886, Appendix B, pp. 592-596), in Mr. F. S. Emmons's report on "The Geology and Mining Industry of Leadville"; and Mr. J. S. Curtis (*Mon. U.S. Geol. Survey*, vol. vii., 1884, pp. 120-138), in his report on "The Silver-Lead Deposits of Eureka, Nevada," has given his method of assaying rocks for traces of gold and silver.

NOTE.—From Sandberger's report it appears that the rocks were treated successively with water, acetic acid, boiling dilute hydrochloric acid for two days, and finally hydrofluoric acid; the several extracts and final residue of fluorides (and pyrite) being separately examined for heavy metals. The products of distillation were also examined. A striking fact observed in all cases was the complete insolubility of the pyrite, even after the severe treatment mentioned. This speaks strongly in favour of the correctness of ferrous iron estimations in silicates by the hydrofluoric and sulphuric acid method when pyrite is present unaccompanied by other sulphides. (See p. 107).

Preliminary Qualitative Analysis.

A complete qualitative analysis of a rock, preceding the quantitative examination is in most cases a sheer waste of time. A few constituents may now and then be specially looked for, but in general time is saved by assuming the presence of most of them and proceeding on that assumption in the quantitative analysis.

Summation of Analytical Results.

As is well known, a complete silicate rock analysis which foots up less than 100 per cent is generally less satisfactory than one which shows a summation somewhat in excess of 100. This is due to several causes. Nearly all reagents, however carefully purified, still contain, or extract from the vessels used, traces of impurities, which are eventually weighed in part with the constituents of the rock. The dust entering an analysis from first to last is very considerable, washings of precipitates may be incomplete, and if large filters are used for small precipitates the former may easily be insufficiently washed.

Given the purest obtainable reagents, an ample supply of platinum, facilities for working, and a reasonably clean laboratory, there is no excuse for failure on the part of a competent chemist to reach a summation within the limits 99·75 and 100·50. Failure to attain 100 per cent in several of a series of analyses of similar nature should be the strongest evidence that something has been overlooked. Excess above 100·5 per cent should be good ground for repeating portions of the analysis in order to ascertain where the error lies, for it is not proper to assume that the excess is distributed over all determined constituents. It is quite as likely, in fact more than likely, to affect a single determination, and one which may be of importance in a critical study of the rock from the petrographic side.

Quality of Reagents.

It is due to say that all analyses performed in the Survey laboratories have been made with the purest reagents obtainable, either by purchase in the open market or by special preparation on the part of manufacturers or in the laboratory. The best acids made in this country are of a high grade, and need no re-distillation except for special experiments. Ammonia has always been redistilled at short intervals; and no sodium carbonate which exceeds 2½ m.grms. of total impurity in 20 grms. (0·012 per cent) is used for the main portions, in which silica, alumina, &c., are to be estimated. For other portions, as phosphoric acid, fluorine, sulphur, a poorer grade is entirely allowable, provided it is free from the element to be determined, and from any other which might interfere with its estimation.

Hydrofluoric acid was always freshly distilled with potassium permanganate until the introduction of ceresine bottles afforded an article sufficiently pure for all but the most exacting work. Care must be exercised even yet, however, that no particles of paraffin or ceresine are floating on the acid, and that the latter is free from traces of chlorine whenever hydrofluoric acid is to be used for bringing the chlorine into solution.

Potassium bisulphate has usually been prepared in the laboratory from sulphuric acid and potassium sulphate, since it is not always to be bought of satisfactory quality. Even then the normal sulphate had first to be examined, for it has been found to contain on different occasions, notable amounts of lead, calcium, and silica.

The phosphorus salt used for precipitating magnesium has been found to contain iron, and calcium is sometimes a constituent of ammonium oxalate. The latter has therefore to be purified or specially prepared, as also oxalic acid, ammonium chloride (in which latter manganese has been observed), and occasionally other reagents. Some hydrogen peroxide contains fluorine, which renders it unfit for use as a chemical reagent.

A "C.P." label is no guarantee whatever of the purity of a reagent; hence no chemicals should be taken on trust because of bearing such a label. Every new purchase should be examined, if it is one in which purity is a desideratum. In general all so-called "C.P." chemicals should at least stand the tests laid down by Krauch ("Die Prüfung der Chemischen Reagentien," 3rd ed., Berlin, Julius Springer, 1896). Of late, the firm of E. Merck, in Darmstadt, has begun to advertise preparations of a certain guaranteed purity, thus inaugurating a long-needed reform in this direction. Even with them, however, the guarantee should be checked, at least until long experience shall have shown the precaution to be superfluous.

To his colleague, Dr. H. N. Stokes, who kindly examined the original draft of this paper, the writer is indebted for several suggestions which have been made free use of in the foregoing.

ON SOME COMPOUNDS OF TRIVALENT VANADIUM.*

By JAMES LOCKE and GASTON H. EDWARDS.

THE green solution obtained when vanadic acid is reduced by nascent hydrogen has been but very slightly studied. That it contains salts of vanadium in the trivalent state was recognised by Roscoe (*Ann. Chem.* (*Liebig*), *Suppl.*, vii., 78), in the course of his elaborate investigation on the chemical nature of this element. Roscoe, however, made no attempt to study the products which could be obtained from the solution which he prepared by dissolving the anhydrous chloride, VCl_3, in water, and failed to make any comparison between that body and the chlorides of other trivalent elements.

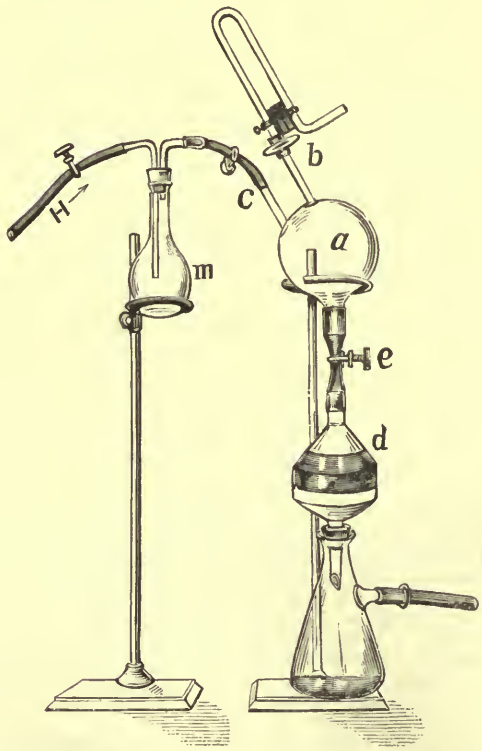
The first compounds to be isolated from a vanadic solution were prepared by Peterson (*Journ. Prakt. Chem.* (2), xl., 44, 1889), who examined in a very thorough manner the fluoride and its double salts with the fluorides of other metals. His results pointed to a close resemblance between vanadium sesquioxide and its derivatives and the compounds of the groups formed by aluminium, chromium, manganese, and iron. Thus, the compound $K_2VF_5.H_2O$ exhibits in its general properties, solubility, &c., close similarity to the analogously constituted salts of aluminium, iron, chromium, and manganese. Ammonium vanadifluoride, $(NH_4)_3VF_6$, is isomorphous with the ferric salt, $(NH_4)_3FeF_6$, described by Marignac (*Ann. Chim. Phys.*, (3), lx., 306), and Petersen prepared other members of the series in $(NH_4)_3CrF_6$ and $(NH_4)_3AlF_6$. A similar relation was observed between double salts with

* From the *American Chemical Journal*, xx., No. 7.

the fluorides of divalent metals, such as $CoVF_5.7H_2O$, $CoCrF_5.7H_2O$, &c.

Petersen's work and the conclusions drawn from his results were further substantiated by the recent investigations of Piccini (*Ztschr. Anorg. Chem.*, xi., 106; xiii., 441) on the alums of vanadium. He succeeded in isolating the salts $NaV(SO_4)_2.12H_2O$, $KV(SO_4)_2.12H_2O$, $NH_4V(SO_4)_2\ 12H_2O$, $RbV(SO_4)_2.12H_2O$, $CsV(SO_4)_2.12H_2O$, and $TlVSO_{42}.12H_2O$, With the exception of a short article by Brierly (*Journ. Chem. Soc., London*, xlix., 822), who prepared a vanadium sulphuric acid, or "alum acid"* $V_(SO_4)SO_4H.4H_2O$, the above investigations embrace practically all that has been published on vanadic salts.

We have recently undertaken the preparation of a number of other compounds, the analogues of which are of characteristic nature in the case of chromium, in the hope of ascertaining more definitely the influence which the atomic weight of vanadium exerts upon the development of the properties common to the compounds of the group: aluminium, vanadium, chromium, manganese, iron, and cobalt.



The chief difficulty which an investigation of this kind presents lies in the extreme readiness with which vanadic solutions absorb oxygen, with formation of vanadyl salts. Petersen was able to start directly from the anhydrous sesquioxide, which is soluble in hydrofluoric acid. The solutions of vanadic sulphate used by Piccini in the preparation of the alums were obtained simply by the electrolysis of vanadic acid in a solution of sulphuric acid. These methods, while satisfactory in individual cases, are of course limited in their applicability, and they could not be used in the preparation of such compounds as a vanadicyanide, sulphocyanate, or the like. We were therefore compelled to start out from the readily oxidisable vanadic hydroxide, precipitated by an alkali after the reduction of the pentoxide with sodium amalgam.

* Chromium is the only other alum-forming metal which yields such an acid, $Gr(SO_4)SO_4H$.

In order to protect the hydroxide and solutions from oxidation, all operations were carried out in an atmosphere of hydrogen. For this purpose the apparatus shown in the accompanying figure was employed. The pear-shaped bulb *a*, of which we had several pieces, holds about 500 c.c. Over its drawn-out end, which is two-thirds of an inch in diameter, passes a piece of thick-walled, soft-rubber tubing, which can be closed by a stop-cock *e*. The tube *b* is of capillary diameter, fitted with a glass cock, and bent over on itself, to more securely prevent the entrance of air when this cock is open. *c* is a somewhat wider tube, which serves for the introduction of reagents, and is closed by a stop-cock when necessary.

For heating on the water-bath, the bulb is placed on the latter, mouth downward, while a rapid current of hydrogen is passed in at *c*, *a* being open. The contents of the bulb may be boiled in a similar manner, the bulb then resting on its side. Reagents are added by means of a small flask *m*, fitted with a cork holding two short tubes, one of which is connected with the hydrogen generator. The reagent having been introduced into the flask (a test-tube is also convenient) the air in the latter is displaced by hydrogen, and the second tube then connected with *c*. The flask is then simply inverted, whereupon the reagent runs into the bulb.

The most important and difficult operation involved in the work was of course the filtration and washing of the vanadic hydroxide. To perform this without exposing the substance to the air, a Buchner's funnel was used, to which was joined by a wide rubber band a well-fitting piece of apparatus, *d*, like an inverted funnel. The stem of the latter was of the same diameter as the mouth of the bulb. Before attaching this filtering apparatus to the bulb, it was entirely filled, together with the suction-flask, with water, and the latter then displaced by hydrogen. Connection was then made, slight suction applied, and the stopcock at the mouth of the bulb opened. The precipitate was washed with water from which the air had been expelled by boiling, from a flask connected as for the introduction of reagents.

When the next operation involved the solution of the precipitate in an acid, the filtrate was drawn off by suction through the pump, the suction-flask rinsed with the water from one or two additional washings, and the acid then introduced as above. The solution was then transferred, either to another bulb, or, if it was to be evaporated to crystallisation, to a crystallising-dish, the side tube of the suction flask being in that case held below the surface of some benzene placed in the dish.

By taking proper care in the observance of minor details, such as the filling of the tubes with water before making connections, &c., we were able almost entirely to obviate the danger of oxidation; and after a little practice we could carry out the operations of filtration and the like almost as rapidly as in the open air. In one afternoon, starting out with vanadium pentoxide, we have prepared vanadium dihydroxide, $V(OH)_2$, washed it, redissolved in hydrochloric acid, and brought the solution into a desiccator. In spite of all the operations subsequent to the reduction of the vanadic acid, the final solution possessed the true lavender colour of vanadious salts, without a trace of green or brown. Roscoe describes such a solution as being a more sensitive reagent towards oxygen than is pyrogallol itself.

The vanadium preparations which we used in this work were placed at our disposal through the kindness of Prof. Paul Jannasch, of Heidelberg, Germany. They consisted chiefly of thoroughly purified vanadates of sodium and ammonium. These compounds were worked up as follows: Enough of the substance to yield about 5 grms. of vanadium hydroxide was dissolved in a small quantity of water, 10 c.c. of concentrated hydrochloric acid were added, and the solution boiled with alcohol to reduce the vanadic acid to vanadyl dichloride, $VOCl_2$. After the alcohol had been driven off, the solution was transferred to a bulb, and while a rapid current of hydrogen was led

through the latter, 5 per cent sodium amalgam was gradually introduced in small lumps, the solution being in the meantime kept acid by the occasional addition of hydrochloric acid. The reduction was continued until the solution just began to lose the pure green colour of the vanadic salts and assume a bluish-green tint, due to compounds of the next lower degree of oxidation. The operation required the addition of about 700 grms. of amalgam.

The mercury was next drawn off, the solution filtered, transferred to another bulb, and treated in the cold with just enough ammonium hydroxide to precipitate the vanadic hydroxide* completely. The latter comes down as a dirty green flocculent precipitate, which absorbs oxygen with the greatest avidity. It was allowed to stand for some time, and then filtered and washed thoroughly with warm water from which the air had been expelled. From this precipitate the following salts were obtained by solution and crystallisation.

Vanadium Trichloride, $VCl_3 \cdot 6H_2O$.—Halberstadt (*Ber. d. Chem. Ges.*, xv., 1619, 1882) mentions the fact that when the anhydrous chloride, VCl_3, is dissolved in water and the solution evaporated over sulphuric acid, a very unstable crystalline compound is obtained. Piccini mentions in a footnote to his first article on the vanadium alums (*Ztschr. Anorg. Chem.*, xi., 107, 1896) that he had obtained this substance in distinct crystals, and found it to have the above composition. This footnote escaped our notice when first reading his article, and at the time of preparing the compound we supposed we were the first to have isolated it. As, however, nearly three years have elapsed since his article was sent in for publication, we may be allowed to describe the compound, yielding to him the priority of its discovery.

It is obtained by dissolving vanadic hydroxide in concentrated hydrochloric acid, and evaporating the green solution to dryness in a vacuum-desiccator. The salt separates out from the syrupy liquid in large green prisms, some of which attained with us the length of nearly half a centimetre. It dissolves in water with extreme readiness, yielding, like the other neutral vanadic salts, a brown solution which becomes green on acidification. The salt is very deliquescent, and on exposure to the air for any length of time dissolves in the water absorbed, and is oxidised to vanadyl dichloride. It is readily soluble in both alcohol and ether, but no distinct crystals could be obtained from its solution in these liquids.

In the analysis of the substance the solution was acidified with nitric acid and the chlorine precipitated with silver nitrate. The vanadium was determined in another portion by titration from the tetravalent to the pentavalent state with iodine, according to Browning's method (*Ztschr. Anorg. Chem.*, i., 158). The water was estimated by difference :—

	Calculated for $VCl_3 \cdot 6H_2O$.	Found.
V	19·24	18·96
Cl	40·10	39·95
H_2O	40·66	41·09
	100·00	100·00

An attempt was made to measure the crystals, but they proved too hygroscopic. Their optical properties, however, were found to conform to the rhombic system. Salts of composition similar to that of this compound are seen in $AlCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, and $FeCl_3 \cdot 6H_2O$.

Potassium Vanadichloride.—An attempt was made to prepare from the chloride a double salt analogous to those of the series $R_2FeCl_5 \cdot H_2O$, in which R is K, Rb, NH_4, &c. A few grms. of the trichloride were dissolved in concentrated hydrochloric acid, the calculated quantity of potassium chloride added, and the mixture left to crystallise in a vacuum. The product consisted chiefly of green crystals of a somewhat lighter shade than that of the pure vanadium chloride, but it was impossible to isolate these completely. A vanadium determination, made in as pure a product as we could obtain, showed that it contained 22·41 per cent V. The quantity calculated for the anhydrous compound $KVCl_4$ is 22·03 per cent V.

Vanadium Bromide, $VBr_3 \cdot 6H_2O$.—This compound was prepared in a manner strictly analogous to that by which the chloride was obtained, pure concentrated hydrobromic acid being used. It crystallises with less readiness than the chloride, and decomposes more easily. In other respects the two compounds were closely similar. The bromide decomposes more or less on solution in water, leaving as a residue a small quantity of a brown substance, probably a basic bromide. Like the chloride, it is soluble in both alcohol and ether, to a green solution. The analysis was carried out as in the case of the chloride.

	Calculated for $VBr_2 + 6H_2O$.	Found.
V	12·83	12·62
Br	60·10	59·65
H_2O	27·07	27·73
	100·00	100·00

The iodide could not be obtained. Vanadium hydroxide dissolves in hydriodic acid as readily as in hydrochloric or hydrobromic, but the solution turns brown on evaporation and eventually leaves only an amorphous, brownish-black residue, only partially soluble in water.

Potassium Vanidicyanide, $K_3V(CN)_6$. — For the preparation of this compound, it was found more convenient to start out from the anhydrous vanadium trichloride, which we prepared according to the method of Halberstadt (*Ber. d. Chem. Ges.*, xv., 1619, 1882). About 5 grms. of this substance were dissolved in as little water as possible* and slightly acidified with hydrochloric acid. A concentrated solution of potassium cyanide containing about one and a half times the calculated quantity of the salt was placed in a bulb, and the vanadium chloride solution then added. The mixture at once assumed the form of a thick, deep purple paste, which gradually became thin again, though without at first losing its colour, and remaining almost opaque. This part of the reaction was observed by Petersen (*J. Prakt. Chem.*, xl., 50), who states that he thus obtained a dark blue solution. The blue colour, however, is in fact due only to very finely divided particles of the original precipitate suspended in the solution, which is itself of a deep wine colour. After shaking for some time the liquid cleared, and only a few flakes of a brown residue, presumably the hydroxide, remained undissolved. It is absolutely necessary to have a considerable excess of potassium cyanide present, as the precipitate dissolves with great difficulty, and a clear solution cannot otherwise be obtained.

The wine-coloured solution, after being filtered, was treated with just enough alcohol to bring about incipient precipitation, and then allowed to stand for some hours surrounded by ice-water. A fine precipitate separated out, which consisted of a mixture of potassium cyanide and vanadicyanide, and, in addition to this, comparatively large crystals of the latter collected on the sides and bottom of the vessel. These alone were saved, the rest of the product being removed by lixiviation. The crystals were repeatedly washed by decantation with 95 per cent alcohol, and finally with ether, and dried in a vacuum-desiccator.

(To be continued).

* Potassium hydroxide does not work as well for this purpose, as it dissolves more or less of the vanadic hydroxide.

* The formation of the hydrated chloride is readily seen when a quantity of the anhydrous chloride is added to about its own volume of water. It dissolves with a hissing sound, and, on cooling, the liquid solidifies to a green crystalline mass. On addition of more water, this dissolves to a brown solution.

MISCELLANEOUS.

Deterioration of Paper.—The Report of the Committee of the Society of Arts on the Deterioration of Paper has now been published, price 1s., and can be obtained on application to the Secretary, Society of Arts, John Street, Adelphi, W.C. Two Appendixes are printed with the Report:—1. Abstracts of Papers on German Official Tests, 1885—96. 2. Précis of Correspondence.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2028.

STANDARDS OF PURITY FOR SEWAGE EFFLUENTS.*

By Dr. S. RIDEAL, D.Sc.(Lond.), F.I.C.

The progress made within the last few years in the bacterial processes for the treatment of sewage has drawn into question the interpretation of analytical results as well as the different standards of purity, by which effluents are to be judged to be acceptable or otherwise. At the present time some consensus of opinion is absolutely necessary.

Opinions have in many cases been founded almost solely on the permanganate process of oxidation, which has the advantage of being easy and rapid in execution, but is open to the following objections:—

1. So many modifications have been introduced in procedure, that the figures obtained by different observers are seldom comparable, as instanced in the recent discussion at Manchester.

2. It mainly measures the carbonaceous matters, which are not the most dangerous.

3. It is incomplete even in measuring these, since many of them are very resistant to permanganate if used, as ordinarily, at low temperatures. For this reason I prefer to work at a higher temperature—namely, that of a water-bath at about 80° C.

4. The interference of nitrites, which are abundant in certain stages of purification, of high chlorides, and of iron and manganese salts derived from a chemical treatment, has not been satisfactorily eliminated, even by the adoption of time limits, such as three minutes, fifteen minutes, two and a half or four hours.

In perfectly fresh human excreta, taking both solids and liquids together, the amount of nitrogen somewhat exceeds the chlorine. It is evident that the proportion between them will remain unaltered whatever volume of water be added, provided the water contains only the ordinary small amount of natural chlorine, as long as the nitrogenous matters do not undergo alteration. Therefore the factor expressing the relation between chlorine and nitrogen will be applicable to sewages generally, independent of their dilution. In subsequent changes, while the Cl will remain unaffected, the total nitrogen will suffer diminution, the loss being due to its escape in the form of gases, such as free nitrogen and nitrous oxide. The extent to which this important purification has been effected will be indicated by the above proportion, which I propose to call the "residual ratio," and prefer to express in percentages of the chlorine.

If Cl be the chlorine of the sewage,
N the total nitrogen,
R the "residual ratio,"

the formula will be—

$$R = \frac{N \times 100}{Cl}.$$

In cases of great dilution, or of an excessive amount of chlorine in the water supply, the expression will become—

$$R = \frac{N \times 100}{Cl - W};$$

W being the chlorine in the water. The simpler formula, however, is in general sufficient.

* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

As nitrogen is significant of the more dangerous forms of pollution, a calculation of the ratio between the different forms of nitrogen furnishes more useful information than a mere consideration of its amount, inasmuch as nitrogen compounds when oxidised are harmless, but when unoxidised are liable to occasion smells, and to be in other respects deleterious. A certain quantity of nitrogen is lost as gas during the changes, but the residue will give a minimum measurement of the original sewage strength. The proportion between the oxidised and unoxidised nitrogen will then denote the extent to which the sample has been purified. A judgment can therefore be formed from the sample without an analysis of the original sewage, as the chlorine contents also give a clue to the strength, and thus such a method would have an advantage over the ordinary system of calculating sewage purification, as it obviates the difficulty of obtaining conformable samples. Even where, as I have elsewhere insisted should be done, a correction is made to a standard chlorine value in comparing the sewage entering and the effluent leaving a certain works, the system I suggest will still have great advantages.

As ammonia must be recognised as a preparatory or transition, and not a finished product, it must be considered as part of the residual unoxidised sewage, and only indicates progress towards complete purification, and gives a criterion as to whether a process is working satisfactorily. A large number of the failures in sewage disposal methods have been owing to the effort to obtain by chemical treatment or filtration a liquid from sewage which should bear some resemblance to drinking water; such an end is impossible without impracticable expenditure, time, and space, attended by disastrous breakdowns at intervals. Fortunately methods have been found which by natural agencies allow us to carry the purification to a rational and harmless stage, when such factors as time, light, volume of oxygen, and various life of a river will be more than sufficient to deal with the effluent.

A few examples to show how the percentage of oxidation reveals the purification effected by different agencies may be quoted here:—

	Oxygen consumed.	Parts per 100,000 of nitrogen. As NH_3.	Organic.	Total unoxidised.	As nitrite and nitrate.	Percentage of oxidation.
A raw sewage . ..	6·66	3·0	6·12	9·12	none	none
A filtrate effluent ..	0·78	2·4	0·92	3·32	1·16	26·0
Another ditto. . ..	0·36	0·92	0·44	1·36	1·09	44·5
London river water	0·20	0·0016	0·049	0·051	0·305	86·0
Same filtered.. ..	0·176	none	0·026	0·026	0·254	91·0
Deep well in chalk .	0·013	none	0·008	0·011	0·450	97·6

Furthermore, one has to consider not only the chemical but also the pathogenic qualities, and these are ignored by all existing standards. It is obvious that a very small amount of nitrogen or carbon, if in the form of ptomaines, would be sufficient to condemn an effluent. I have noticed that many dilute putrid sewages of offensive character have shown less albumenoid or organic nitrogen than the condemnatory limits of existing standards, so that these arbitrary rules are of little or no value.

On the other hand, when a sewage has been subjected to nitrification, although the albumenoid ammonia may be higher than the old standards, the presence of nitrate seems to have a beneficial influence upon the quality of such sewage, and under these circumstances a greater quantity of albumenoid or organic nitrogen may be tolerated.

The multitude of bacteria in sewage is so enormous, and their character so various, that a mere counting of their numbers must be unmeaning and inaccurate. The ratios, however, between either those liquefying and not

liquefying gelatin, or between the aërobic and non-aërobic, or between those growing at ordinary temperatures and at blood heat, give much more valuable information.

Whilst therefore any absolute number as a standard is undesirable, only a low number of organisms of the Coli group should be permissible in an effluent, with an absence of dangerous pathogenic forms.

Absolute sterility in an effluent is at present out of the question, nor in general would it be necessary or even advisable, inasmuch as subsequent organic improvement would be prevented, but the destruction of pathogenic forms could be completed by a "finisher" like chlorine when special danger was present.

Dr. Dupré some years ago introduced a method of ascertaining the condition of healthiness or otherwise of an effluent by enclosing it in a bottle and determining the free oxygen present before and after keeping. This seems a natural way of carrying out the "oxygen consumed" test. He observes (*Analyst*, August, 1898) :—"Pure water remained aërated when bottled up, but water containing sewage de-aërated itself. An effluent that did not appreciably de-aërate itself might be admitted anywhere without fear of putrefaction." Unfortunately, although the actual work of this test can be carried out in a few minutes. the sample had to be allowed to stand for five to ten days,

On similar—but less natural—lines, the "Incubator Test," adopted in the Manchester report on systems of sewage purification, maintains an effluent by itself at a warm temperature (five days at 80° F.), and determines the oxygen absorbed in three minutes before and afterwards, at the same time noticing any change of odour. The result is, however, again arbitrary, as an effluent is not intended to be stored by itself, but, when finished, to be discharged at once into water which is moving and aërated.

The results seem to be more favourable to effluents which have been sterilised by a chemical or precipitation process, but which have notoriously in many cases given rise to a subsequent nuisance, than to those containing the materials, bacterial and chemical, for rapid self-purification in a river.

Mr. Dibdin has recently put forward this test, which he describes as follows:—"He had long since adopted in his own mind a physiological standard, viz., that the quality of an effluent should be such that fish could live healthily in it, . . . such a definition involves necessarily the absence of poisons and the presence of oxygen." But while an effluent which kills fish is obviously unhealthy, it does not follow that one where fish will live is therefore a good one. It is well known that fresh-water fish are gross feeders, and fish in large numbers are often seen to congregate at the mouths of sewers where fæcal matter is visibly floating, being attracted by the fragments of food and insects carried down by the sewage. Fish, in fact, are more affected by muddy water and by chemicals from factories than by excreta.

Amongst the standards which have been proposed in the past, or have been adopted by local bodies, are the following, some of which have been repeatedly quoted in papers on the subject, while others are gathered tentatively from published documents, or from a consideration of decisions in disputed cases. None of them, however, have strictly the force of law; in fact, some have actually been disclaimed by the bodies to which they were attributed. The proportions are parts per 100,000:—Rivers Pollution Commissioners—Organic carbon, 2·0; organic nitrogen, 0·3. Thames Conservancy—Organic carbon, 3·0; organic nitrogen, 1·1. The Thames Conservancy state that they require a higher standard for effluents just above the intakes of the water companies than for those below. Derbyshire County Council—Albumenoid ammonia, 0·1; oxygen absorbed, 1·0. Ribble Board—Albumenoid, 0·1; oxygen absorbed, 2·0. Mersey and Irwell—Albumenoid, 0·14; oxygen absorbed, 1·40.

Provisos as to amount of suspended solids, acidity, alkalinity, metals, &c., are inserted in some, and have special reference to manufacturing effluents.

But in all these arbitrary limits, no account is taken of the volume of the river into which the effluents are discharged, although attention was long ago drawn to the purifying action of river water. The London County Council have recognised the fact that an oxidising agent added to the effluent at the time of contact with the river prevents any foulness. Provided, therefore, a river is well aërated, or an effluent is well nitrated, or an oxidising agent is supplied in sufficient quantity at the time of contact, an effluent may contain a larger quantity of organic matter than has been sanctioned in the past, and variations in such quantities are permissible under conditions varied in the above way.

In America, from the work of the Massachusetts State Board of Health, Rudolph Hering fixes a limit to the amount of free ammonia permissible in a stream, and finds that if the flow of the stream is less than 2½ cubic feet per second per 1000 persons (or one gallon per minute per person) "an offence is almost sure to arise"; but when the flow is greater than 7 cubic feet per second per 1000 persons, then safety is assured.

"In other words, when the free ammonia is greater than 0·12 part per 100,000 the conditions are probably objectionable." I find that these limits correspond to about 50 volumes of river water to average sewage in this country, and it is obvious that such conditions are only possible under very special circumstances, and the limit is much greater than we have found necessary in England.

Some time ago, in conversation with Mr. Henry Law, we arranged the following formulæ for the conditions of discharge into a stream. The basis I prefer to take is the same as that preferably adopted for waters, viz., 100 litres or 100,000 parts:—

Let X be the flow of the stream in 100 litres per minute.

O = grammes of free oxygen in 100 litres.

S = number of hectolitres of effluent discharged per minute.

M = grammes of oxygen required to consume the organic matter in 100 litres of effluent, as determined by the permanganate test after deducting that required by nitrites.

N = grammes of available oxygen as nitrate and nitrite per 100 litres.

This latter factor requires explanation. Warington, Munro, Gayon, and Dupetit, Adeney, and others, have shown that, always with the help of bacteria, the oxygen of nitrates and nitrites is available for the burning up of organic matter. In my own experiments I have found that the large loss of organic nitrogen noticed so frequently in analyses of sewage in progressive stages of change was not accounted for by the production of nitrous acid, of ammonia, or of nitrogen gas. Gayon and others have observed the formation of nitrous oxide, which, from its solubility and vague reactions, would ordinarily escape observation. Therefore, to be on the safe side, I have allowed for the available oxygen 2 atoms of O for every HNO_3, *i.e.*, N_2O_5 to N_2O, and 1 atom for HNO_2, or N_2O_3 to N_2O.

The quantity of free oxygen in the stream will then be XO, and that required by the effluent will be S(M − N).

Putting C as the ratio between the amount of oxygen in the stream and that which is required to oxidise the organic matter in the effluent,—

$$XO = C(M - N)S.$$

Where there are no nitrates in the fluid,—

$$XO = CMS.$$

If N be less than M, M − N = the deficit of oxygen in the effluent, requiring to be supplemented by the free oxygen in the river, such an effluent will throw a burden on the river, and cannot be considered in a satisfactory

state; and it will be a question of volume and other circumstances whether it can be permitted to be discharged at all. Where XO is greater than (M – N)S there will be a chance of the stream dealing with the inflowing liquid; where the reverse is the case the addition must necessarily cause foulness.

In favourable cases, where bacteria and algæ are active, and the oxygen of the river is able by their help to deal rapidly with the incoming residues, the minimum ratio between the volume of the stream and the volume of effluent that could be allowed to be discharged into it would be indicated by the value of C in the above equation, which would also approximately denote how far the population might increase before the proportion would be seriously disturbed.

The minimum figure will be reduced by the nitrites or nitrates of the river water itself, and by the free oxygen which may be present in the effluent. River water may have 90 per cent of its nitrogen oxidised, and, when saturated, contains about 700 c.c., or, approximately, 1 grm. of free oxygen per 100 litres. We may assume that with the almost unlimited exposure and admixture in a flowing river, the common natural bacteria that work the changes are certain to be present. Hence, in theory, comparatively few volumes of a river water are necessary for supplying the oxygen requisite for even a raw sewage after its solids have been removed by filtration or subsidence. From this cause it is a common observation that the dissolved impurity remaining in a stream is a mere fraction of that in the volumes of sewage that have entered it in its upper course.

But from the factor of time, and the inadvisability of denuding the river of its oxygen, which might be only gradually renewed from the air, it is necessary with the raw liquids of sewage to allow a considerably larger proportion of river water than the minimum above calculated. Dupré states that admixture with about 30 volumes of fully aërated river water prevents sewage from becoming foul, and ultimately purifies it. I have found the same result from a less quantity.

Where the organic matter is well fermented, and the liquid advanced in nitrification, as in properly managed septic effluents, the case is far more favourable. Here, in the above equation, N is greater than M, and there is a surplus of available oxygen in the effluent—that is to say, an effluent of this kind not only does not absolutely require any dilution with river water, as containing within itself the elements of its own purification, but by its surplus oxygen is capable of actually improving the river into which it enters. This apparently paradoxical result in cases of polluted streams is paralleled by the effect of the addition of artificial oxidising agents, such as that of manganate of soda to the Thames at Crossness. In healthy effluents the quantity of available oxygen, N, in the above equation, is far higher than could be supplied by any process of mere aëration.

As an example of the application of the formula XO = C(M – N)S, we may cite two rivers, the Thames and the Exe:—

	X.	O.	M.	N.	S.	C.
Thames ..	1100	0·4	4·3	0·23	100	1·08
Exe	47	1·0	6·66	1·16	1·084	7·9

X and S are stated in million gallons.

The formula shows that the Thames with C = 1·08 has so narrow a margin of effective natural oxidation that it has often had to be supplemented, especially in warm weather, by the addition of chemicals. In the Exe, on the other hand, with C = 7·9, there is a large margin for natural purification.

But we cannot, as a rule, throw the burden of the final changes on the stream on account of the time taken and the odours and deposit that generally ensue. On the other hand, an effluent that is in an active state of wholesome bacterial change, under the above conditions of free and potential oxygen, will conform to Adeney's proposed test:—"The limit of impurity to be allowed in a water should be such, that when a given volume of it is mixed with a given volume of fully aërated river water, and the mixture kept out of contact with air, a decided oxidation of the ammonia originally present into nitrous or nitric acid shall be indicated." . . . It will be noticed that this test is practically that suggested by Dupré many years ago. Such an effluent, as experience teaches, if clear and nearly free from odour, may be safely discharged into any river of moderate volume.

THE ACTION OF LIGHT UPON DYED COLOURS.*

The Report of the Committee presented this year refers to the results obtained during the year 1896-7, in which period a large number of wool and silk patterns, dyed with various natural and artificial *brown* and *black* colouring matters, were exposed to light.

It is with regret that the Committee have to announce the death of James A. Hirst, Esq., in whose grounds at Adel, near Leeds, all the patterns experimented upon since 1892 have been exposed. Mr. Hirst took great interest in the work of this Committee, and the same interest is shown by his son, E. A. Hirst, Esq., who has expressed the pleasure it gives him in being able to aid in the continuation of the work.

The general method of preparing the dyed patterns and the manner of exposing them under glass, with free access of air and moisture, were the same as already adopted in previous years.

Each dyed pattern was divided into six pieces, one of which was protected from the action of light, while the others were exposed for different periods of time. These "periods of exposure" were made equivalent to those adopted in previous years by exposing, along with the patterns, special series of "standards," dyed with the same colouring matters as were then selected for this purpose. The standards were allowed to fade to the same extent as those which marked off the "fading period" in previous years, before being renewed, or before removing a set of dyed patterns from the action of light. The patterns exposed during 1896-7 are, therefore, comparable, in respect of the amount of fading action to which they have been submitted, with the dyes already reported upon.

The patterns were all put out for exposure on July 22, 1896, certain sets being subsequently removed on the following dates:—August 22, September 29, November 5, 1896; May 22, September 6, 1897. Of these five "periods of exposure" thus marked off, periods 1, 2, 3 were equivalent to each other in fading power, whereas periods 4 and 5 were each equivalent to *four* of the first period in this respect; hence five patterns of each colour have been submitted respectively to an amount of fading equal to 1, 2, 3, 7, and 11 times that of the first "fading period" selected—viz., July 22 to August 22, 1896.

The dyed and faded patterns have been entered in pattern-card books in such a manner that they can be readily compared with each other.

The following tables give the general result of the exposure experiments made during 1896-97, the colours being divided, according to their behaviour towards light, into the following five classes: Very fugitive, fugitive, moderately fast, fast, very fast.

The initial numbers refer to the order of the patterns in the pattern-books. The S. and J. numbers refer to Schultz and Julius's "Tabellarische Uebersicht der künstlichen organischen Farbstoffen."

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* Report of Committee, consisting of Dr. T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Bristol Meeting, 1898.

In the case of colouring matters requiring mordants, the particular mordant employed is indicated in brackets after the name of the dye-stuff.

The colours marked thus (*) appear to be somewhat faster than the rest of the class in which they are placed.

Brown Colouring Matters.

Class I.—Very Fugitive Colours. (Wool).

The colours of this class have faded so rapidly that at the end of the first "fading period" (July 22 to Aug. 22, 1896) only a very faint colour remains, or it has become very materially altered in hue. At the end of the fifth period (about one year) all traces of the original colour have disappeared, the woollen cloth exhibiting merely a yellowish, brownish, or greyish tint, according to the colour of the original pattern.

Azo Colours.

Wool Book XII.

Basic Colours.—

1. Leather Brown R. Constitution not published.
2. Chrysoïdine AG. From aniline and *m*-phenylenediamine. S. and J. III. 16.
3. Chrysoïdine FF. From aniline and *m*-toluylenediamine.
8. Leather Brown V. Constitution not published.

Direct Cotton Colours.—

1. Titan Brown Y. Constitution not published.
2. Benzo Brown 5R. From primuline and phenylenediamine. S. and J. III. 110.
*4. Cloth Brown (red shade). From benzidine, salicylic acid, and α-naphthol-sulphonic acid NW. S. and J. III. 193.
13. Benzo Brown G. From sulphanilic acid and Bismarck Brown. S. and J. III. 273.
25. Hessian Brown MM. From sulphanilic acid, tolidine, and resorcinol. S. and J. III. 278.

Azoxy Colours.

Wool Book XII.

Direct Cotton Colours.—

21. Mikado Brown M. Constitution not published.

Notes.—In the case of Chrysoïdine AG and FF, and Cloth Brown, the colours alter very rapidly during the first "period of exposure," the altered colours then fade more slowly, without any further change in hue.

Class II.—Fugitive Colours. (Wool).

The colours of this class show very marked fading at the end of the second "fading period" (August 22 to September 29, 1896), and after a year's exposure they have entirely faded, or only a brownish, drab, or grey tint remains.

Azo Colours.

Wool Book XII.

Acid Colours.—

1. Resorcin Brown. From *m*-xylidine, sulphanilic acid, and resorcinol. S. and J. III. 163.
2. Fast Brown G. From sulphanilic acid and α naphthol. S. and J. III. 165.
4. Acid Brown G. From aniline and *m*-diamido-azobenzene-*p*-monosulphonic acid. S. and J. II. 136.
7. Naphthylamine Brown. From naphthionic acid and α-naphthol. S. and J. III. 92.
8. Sulphamine Brown. From α-naphthylamine and nitroso-β-naphthol-sodium-bisulphite. S. and J. III. 57.
9. Acid Brown R. From naphthionic acid and Chrysoïdine. S. and J. II. 91.
10. Alkali Brown. From Primuline and *m*-phenylenediamine. S. and J. III. 110.
11. Fast Brown 3B. From β-naphthylamine-sulphonic acid Br and α-naphthol. S. and J. III. 103.

Wool Book XIII.

Basic Colours.—

*1. Chrome Brown RO (Cr). From naphthionic acid and α-naphthol. S. and J. III. 92.
*2. Chrome Brown BO (Cr). Constitution not published.
*3. Chrome Brown R (Cr). Constitution not published.
4. Nut Brown. From *m*-toluylene-diamine and *m*-toluylene-diamine. S. and J. III. 174.
*5. Bismarck Brown 2G. From *m*-phenylene-diamine and *m*-phenylene-diamine. S. and J. III. 172.
*6. Leather Brown. From amido-*p*-acetanilide and *m*-phenylene-diamine; products treated with HCl. S. and J. III. 160.
*7. Leather Brown O. Similar to Leather Brown.

Direct Cotton Colours.—

8. Diazochromine BS. Constitution not published.
11. Toluylene Brown R. From sulphanilic acid and Bismarck Brown sulphonic acid.
15. Direct Brown Y. From *m*-amido-benzoic acid and Bismarck Brown. S. and J. III. 275.
19. Cloth Brown (yellow shade). From benzidine and salicylic acid and dioxy-naphthalene (2·7). S. and J. III. 194.
26. Catechu Brown. From Bismarck Brown and *m*-phenylenediamine. S. and J. II. 220.
27. Congo Brown VBB. Constitution not published.
*28. Catechu Brown DDX. Constitution not published.
*29. Catechu Brown DDDX. Constitution not published.
*30. Hessian Brown B. Constitution not published.
*31. Azo Brown. Constitution not published.
*32. Toluylene Brown R. Constitution not published.
*33. Benzo Brown. Constitution not published.
*34. Benzo Brown BR. Constitution not published.
*35. Benzo Brown B. From naphthionic acid and Bismarck Brown. S. and J. III. 274.
*36. Benzo Brown NB. Constitution not published.
*37. Toluylene Brown M. Constitution not published.
*38. Toluylene Brown B. Constitution not published.
*39. Cotton Brown A. Constitution not published.
*40. Cotton Brown N. Constitution not published.
42. Toluylene Brown VO. Constitution not published.
44. Toluylene Brown 2BO. Constitution not published.
46. Benzo Black Brown. Constitution not published.
47. Sulphon Brown R. Constitution not published.
*48. Sulphon Dark Brown. Constitution not published.

Direct Cotton Colours Developed.—

2. Diazo Brown R (extra). Constitution not published. Azotised and developed with β-naphthol.
*3. Zambesi Brown G. Constitution not published. Azotised and developed with toluylene-diamine.
4. Diazo Brown G. Constitution not published. Azotised and developed with β-naphthol.
5. Zambesi Brown 2G. Constitution not published. Azotised and developed with toluylene-diamine.
6. Diazo Brown Y. Constitution not published. Azotised and developed with β-naphthol.
7. Diazo Brown V. Constitution not published. Azotised and developed with β-naphthol.
*8. Diamine Brown V. From benzidine and amido-naphthol-sulphonic acid and *m*-phenylene diamine. S. and J. III. 182. Azotised and developed with phenylene-diamine.

Natural Colouring Matters.

Mordant Colours.—

6. Sanderswood (Cr). Pterocarpus santalinus (wood).
7. Barwood (Cr). Baphia nitida (wood).
*8. Ventilago (Cr). Ventilago madraspatana (root-bark).
10. Camwood (Cr).
11. Limawood (Cr) (Cu). Cæsalpinia echinata (wood).
*13. Catechu (Cr). Areca Catechu (extract).

NOTES.—Leather Brown and Leather Brown O might almost equally well be classed as "moderately fast" colours. In the first "fading period" they become somewhat greyish in hue, but the altered colour fades very gradually, leaving at the end of a year a fairly good drab-grey colour.

(To be continued).

ORGANIC MATTER IN BURNT CLAYS AT HIGH TEMPERATURES.

By ROBERT MELDRUM, F.C.S.

DURING many years my attention has repeatedly been attracted to a green or yellowish-green colour which often appears on porous clay ware after being saturated with water and allowed to dry. This colour often appears on terra-cotta, battery cells, crucibles, drain-pipes, fire-clay bricks, and indeed on nearly all kinds of porous clay ware. At first I formed the opinion that it was due to bacteria or microscopical fungi; this view I held till a favourable opportunity presented itself for a practical examination of the matter. For this purpose white battery cells and red terra-cotta which had been fired recently were selected for the experiments. These were coarsely ground, and from 100 to 200 grms. taken and repeatedly treated with fresh distilled water till no reaction was given for sulphates. The water extract, which measured about 700 c.c., had a distinctly yellow colour, similar to a weak solution of bichrome, and had a very strong earthy smell: this was slowly evaporated, during which numerous small bubbles were given off, which I thought to be very characteristic of these extracts. About 2 c.c. of this gas was collected, but no definite information was obtained as to its nature. On boiling the liquid down to small bulk the smell disappeared, which seems to indicate that the odoriferous principle is a volatile substance. It is remarkable that this same colour is evolved from the filtrate from fossil meal and many porous stones. The highly concentrated extract has a bitter taste, but sometimes sweet. The total soluble matter in burnt clay I have found to vary between 2·94 to 25 grains per lb., after drying at 200° C., which consists mainly of calcium sulphate and chloride, sodium sulphate and chloride.

The following results were obtained from samples of burnt terra-cotta:—Total soluble matter, 11·9, 25·3, 2·94 grains per lb. respectively. No. 2 contained 35·91 per cent SO_3, 12·38 per cent CaO, 5·24 per cent $Al_2O_3.Fe_2O_3$, 1·60 per cent insoluble, 14·12 per cent Na_2O; the analysis could not be completed as all the liquor was exhausted. When the extract was evaporated to dryness it still appeared transparent and slightly yellow in colour; on increasing the heat it became opaque and gave off very pungent vapours smelling like burning fats, but with a sweetish smell of burnt sugar; and on further raising the temperature most irritating and dense vapours were evolved, the residue turning black, which did not yield a yellow colour to water, but on heating with HCl gave strong reaction for iron.

A concentrated extract from battery cells was examined with the following results:—$K_4Fe(CN)_6$, no result; $K_3Fe(CN)_6$, no result; KCNS, no result; H_2S, no result; $(NH_4)_2SO_4$, no result; HCl discharged colour, but was recovered by addition of NH_4HO; KI, no result; $SNCl_2$, discharged colour; $AgNO_3$, almost precipitated the yellow colouring matter along with the chlorine, the precipitate being of a flesh colour; pyrogallic acid gave indigo-blue colour, changing to greenish-blue, this being a very delicate reaction; tannic acid gave bluish-black colour, appearing almost black; sodium phosphate, no change; K_2CO_3, no change; the colour was insoluble in 30 per cent benzol and petroleum.

This examination, though very incomplete, is yet sufficient to indicate that the colouring-matter is an organic salt of iron. All these clays were fired for long periods in an oxidising atmosphere of more or less intensity at temperatures of not less than 700° C., though I have obtained similar extracts from fire-clay ware fired at a temperature of over 1000° C. An apparent satisfactory explanation of this is the absorption of products of combustion during the cooling of the red-hot ware; but it must be remembered that ware fired in muffles, and protected as much as possible from these, also yield extracts containing organic matter. It has been observed that several white clays yield these yellow extracts previous to being fired, and it therefore appears that the yellow matter is contained in the raw clay, and that it undergoes little decomposition during the firing.

It is my intention to carry on this investigation, as it seems to me that, if these results can be confirmed, a new field of research will be opened up.

THE CYANOMETRIC ESTIMATION OF SOME METALS.*

By HARRY BREARLEY and HORACE JERVIS.

SINCE the use of silver iodide as an indicator in cyanometric estimations was proposed, it has been numerously applied in several branches of analytical chemistry.

Harting says that potassium iodide gives a precipitate with silver nitrate in presence of 30,000 parts of water. In the presence of alkaline salts, especially sulphates, and where the silver nitrate is used to form an opalescence with an excess of potassium iodide, the delicacy of the test is very much heightened. Without exaggeration, this form of indicator may be said to exhibit differences equivalent to one part of nickel, copper, silver, &c., in five million parts of solution.

In estimating nickel salts, say, the cyanide is added until the silver iodide clears up; but, in order that this point shall be exactly coincident with the formation of the double cyanide of nickel and potassium, it is necessary to add the reagent more slowly towards the end. It is general, we believe, where the titrations are numerous to add the cyanide with some levity and then go back with silver nitrate. It may be gathered subsequently that such a procedure is not without its advantages. In going back the silver nitrate may be added either to an agitated liquid, in which case the first observable turbidity may deepen on standing, or by superstratifying the silver nitrate, in which case the turbidity may weaken on standing. In pure solutions these differences—which, of course, right themselves on standing awhile—are not very noticeable; in the presence of some reagents, however, they are emphasised, and it becomes necessary, where speed is a consideration, to adhere to one or the other means of reaching the final indication.

The cyanometric estimation of nickel, probably by comparison with the like estimation of copper, has become notable for the levity with which subsidiary reagents, such as alkalis or alkaline salts, may be added. A point in connection with the potassium iodide, however, deserves notice. Large amounts of KI accentuate the difference noted in the last paragraph. On adding KI to a just cleared solution the turbidity will reappear. Our experience is that the indicator is quicker and more delicate the less potassinm iodide there be used in excess of that necessary to form the working turbidity. The depth of turbidity is a matter of taste, but the addition of 2 c.c. of a 2 per cent KI solution for each 500 c.c. solution titrated provides the deepest desirable cloudiness.

* This paper only partly covers the ground we have mapped out. A temporary but unavoidable delay leads us to present what was already presentable.

The behaviour of nickel and copper salts during cyanometric estimation shows some notable contrasts. The respective behaviour of the two metals in presence of alkalis and alkaline salts has been referred to. It is remarkable that while the theoretical quantity of KCN will complete the reaction with nickel salts, that with copper salts cannot be completed until a considerable excess of the KCN has been added. In presence of nitrates, acetates, tartrates, and sulphates an alkaline solution of copper (chlorides being absent) causes the silver iodide turbidity to blacken and become almost useless; when nickel replaces copper this does not occur. Nickel salts exhibit a peculiarity which, so far as we are aware, has not previously been referred to. The point should be emphasised, on account of the insidious character of the error it may introduce.

Let, say, 50 c.c. of KCN be added to 0·1 grm. of nickel in solution as nitrate or chloride, where about 70 c.c. of KCN is needed to form the double nickel-potassium cyanide. In a minute, or less, a silky crystalline precipitate will begin to form, and in five or ten minutes all, or nearly all, of the uncombined nickel will have been precipitated. Now, as solutions containing unknown amounts of nickel would be titrated carefully and somewhat slowly, it is manifest that to some extent this reaction may take place. The precipitate is soluble in small excesses of KCN, but not very readily so. It is possible, therefore, that when once formed it would escape detection even after the AgI turbidity was cleared up unless it was present in considerable quantities.

An antidote to this undesirable reaction is to be found in ammonium sulphate. A test in all respects like the preceding one, except that ammonium sulphate equivalent to 2 c.c. strong H_2SO_4 was also added, showed only a faint precipitate after standing twenty minutes. Thus, ammonium sulphate serves the double purpose of heightening the iodide turbidity and retarding the formation of the above-mentioned precipitate.

Cyanometric Estimation of Nickel in presence of other Elements.—At one time we thought it reasonable to deduce from the superior behaviour of nickel in so many circumstances, that its behaviour with associated elements would in no case be worse than those exhibited for copper (Chemical News, lxxvi., 291). Our speculations were fouled in attempting the estimation of nickel in presence of aluminium. On this account, and in view of some later work on nickel alloys, we proceeded to observe the interference of some commonly associated elements and to find such means as would overcome them.

The following details are common to each test:—Amount of nickel, 0·1 grm.; interfering metal, 0·05 and 0·1 grm.; excess of ammonia, 10 c.c. (2 normal). The results are summed in the table. The last column (reproduced from Chemical News, lxxvi., 292) shows the percentage error in the like titration of copper. It is feasible to make alkaline with other bodies than ammonium hydrate; the advantageous use of such will be noted in the remarks allotted to each element. Unless otherwise stated, the foreign element was added as a chloride.

Table I.

Metal.	Nickel found. 0·05 grm. added.	Nickel found. 0·10 grm. added.	Per cent error.	Per cent error with copper. Soda salts.	Per cent error with copper. Ammonia salts.
Calcium	0·1000	0·1000	0·0	0·0	0·5
Barium	0·0999	—	0·1	0·0	0·4
Strontium ..	0·1000	0·1002	0·2	0·0	0·0
Magnesium ..	0·1000	0·1002	0·2	0·2	0·2
Zinc	0·1015	0·1021	2·1	2·0	9·4
Cadmium ..	0·1002	0·1003	0·3	0·0	2·8
Aluminium ..	0·0970	0·0956	4·4	0·7	0·7
Iron	0·0989	0·0984	1·6	1·3	0·2
Manganese ..	0·0999	0·1002	0·2	3·0	3·1
Chromic oxide	0·0888	0·0834	16 6	2·5	27·0
,, acid.	0·1003	0·0998	0·2	0·4	—
Tin	—	0·1001	0·1	0·3	0·2
Molybdenum .	0·1000	0·0999	0·1	0·2	0·0
Arsenic	0·1000	0·1000	0·0	0·2	0·2
Antimony ..	0·1000	0·1000	0·0	0·4	0·4
Bismuth . ..	0·1002	0·1001	0·1	0·0	—
Lead	0·1000	0·0999	0·1	0·2	0·0
Uranium . ..	0·1002	0·1001	0·1	0·2	0·4
Tungsten ..	0·0999	0·1000	0·0	—	—

Remarks on the Interferences.

Salts of the alkalis (sodium and potassium) and alkaline earths (calcium, magnesium, strontium, and barium) have no appreciable influence, such as is recorded being conceivably due to experimental error. In the presence of those elements (barium, &c.) which form insoluble sulphates, it is advisable to replace the ammonia sulphate, used to deepen turbidity, by a chloride.

Zinc.—It is found that the interference of zinc decreases as the excess of ammonia increases. On the other hand, if the AgI be cleared and then a measured excess of KCN be added, only a portion of that excess can be active to the silver nitrate which is added to reproduce the turbidity. The more cyanide there is added, the more there is remaining unaccountable to the silver nitrate. This latter fact explains why the copper titration, which necessarily involves a much larger amount of potassium cyanide than is necessary to theoretically complete the reaction should suffer zinc to exert an interference equal to 9·5 per cent, while with nickel the interference is only 2 per cent.

The usual acid titration (see "Aluminium") leaves a discrepancy of 1·3 per cent; but if, after adding the cyanide, we replace the ammonia by soda carbonate, then the zinc becomes for the most part precipitated as carbonate, and only a small portion combines with the excess of cyanide and remains in solution. From this point the procedure is:—Filter off the zinc carbonate through a ribbed paper, and to the filtrate add silver nitrate; it is easy to distinguish between the iodide turbidity and the small amount of zinc carbonate which the silver separates from its cyanide combination, and so it is practicable to note—by the readiness with which the superstratified iodide turbidity disappears, when the solution contains only traces of free KCN. At that point, re-pass the solution through the filter previously used. This operation gives a clear solution in which to observe the end-reaction, and also incorporates the stronger cyanide solutions which were left in the paper and precipitate on the first filtration. With a knowledge of the approximate amount of nickel present, the whole process is very easy and very accurate. The normal titration furnishes the required approximation in a few minutes.

Moore (Chemical News, lix., 292) finds that the titration may be performed in presence of zinc if "to a slightly acid solution there be added an excess of sodic pyrophosphate until the precipitate which at first forms is redissolved to a perfectly clear solution." We must admit that the use of this reagent does improve the results, but our experience is that pyrophosphate alone causes the results to be low, and as the tendency of zinc is to give high results, we consider the betterment of the results on using pyrophosphate to be due, partly at least, to compensatory errors.

Cadmium.—The remarks on the good results of zinc and nickel compared with zinc and copper probably apply also to the cadmium interferences. Where the amount of cadmium was so great as to cause serious error, the acid titration along with soda carbonate might be adopted.

Aluminium.—Where a precipitate is formed in the alkaline liquid, the interference was determined by adding a slight excess of cyanide and filtering off an aliquot portion of the clear filtrate. With aluminium, as well as with other bulky precipitates, we found that the interference varied considerably when the operations were performed in duplicate unless they were carried out in a *precisely* similar way, so that where the amount of aluminium is

known its influence on the results cannot be safely eliminated by any method of allowances.

The titration may be accurately performed by adding cyanide to a faintly acid or neutral solution and then at once adding the usual excess of ammonia, filtering an aliquot portion of the clear liquid, and going back with silver nitrate. A preliminary test is necessary unless one has some knowledge of the amount of nickel present. As this procedure eliminates the interference of other metals which are precipitated in an alkaline solution, we may briefly refer to it as the acid process.

Lecœuvre has published a process (Chemical News, lxxi., 188) for estimating nickel, in which potassium cyanide is added to the neutral solution of the nickel salt until the precipitate previously formed is just dissolved.

Pyrophosphate of soda is not a good reagent to use for preventing the precipitation of the alumina. In a direct titration it causes the iodide turbidity to clear too soon, and if an excess of cyanide has been added, the successive turbidities formed by the silver nitrate gradually disappear. These observations are in a line with those of Moore (Chemical News, lxxii., 92), who, using the pyrophosphate to prevent the precipitation of iron, finds that "the solution once cleared up often becomes troubled again on standing for a minute. A further addition of cyanide must be given until the liquid is perfectly limpid."

Tartaric also introduces the lagging element, but only in a small degree, and when used in large amounts. It is to be preferred, too, because, where large amounts must necessarily be used, the turbidity temporarily cleared quickly recovers itself, and the titration is very little delayed. One-tenth of a grm. of aluminium may be kept in solution by 1 grm. of tartaric acid or less, and five times this amount does not greatly confuse the end-reaction. It is noticeable that in copper titrations pyrophosphate is the better reagent to use for the purpose of preventing the precipitation of bulky hydroxides of the associated metals.

Test Analyses.—The KCN was standardised in each case in the usual way.

Modification.	0·05 grm. Al present.	0·10 grm. Al present.
Acid titration	0·1002	0·1003
Tartaric acid	0·1000	0·1001

Iron.—In our regular experience with nickel-iron alloys, we have invariably found that a cyanometric estimation in presence of iron was low. In such cases as this, the low results are generally accountable to the precipitated iron carrying down portions of nickel, and—by occlusion in its flocks—preventing the cyanide readily reacting with it. Such an explanation suggests that if carbonated alkali were used the results should be improved, because the precipitate is notably more open and easily reacted with. The ammonium carbonate re-dissolves a little of the precipitated iron, and so tends to retard the filtration. Otherwise the process is very satisfactory. The acid titration may also be successfully adopted.

Modification	0·5 grm. iron present.	0·10 grm. iron present.
Ammonium carbonate ..	—	0·1001
Acid titration	0·1001	0·1003

(To be continued).

ON SOME COMPOUNDS OF TRIVALENT VANADIUM.*

By JAMES LOCKE and GASTON H. EDWARDS.

(Concluded from p. 169).

In the analysis of the product the carbon and nitrogen were determined by combustion. The vanadium was estimated by titration with iodine and the potassium as sulphate, in a separate portion, after the oxidation of the vanadium to vanadic acid and its removal as lead vanadate (Roscoe, *Ann. Chem., Liebig, Suppl.*, viii., 102).

	Calculated for $KV(CN)_6$.	Found.
V	15·74	15·89
C	22·22	21·80
N	25·93	26·36
K	36·11	36·47
	100·00	100·52

This salt forms another member of the series of complex cyanides of the formula $K_3M(CN)_6$, of which the other members as yet known are $K_3Cr(CN)_6$, $K_3Mn(CN)_6$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_3Rh(CN)_6$, and $K_3Ir(CN)_6$. The crystals obtained were about a millimetre in length, and of a bright scarlet colour. Owing to their instability it was impossible to measure them, and thus determine whether they were isomorphous with the other members of the series. They appeared under the microscope to be rhombic plates, with well-formed domes and base; in polarised light, however, they showed inclined extinction, and are therefore probably monoclinic like the others. In potassium ferricyanide the angle β is 90° 6'.

Potassium vanadicyanide is readily soluble in water, insoluble in alcohol. Its aqueous solution grows turbid within a few minutes, however, but is much more stable when containing some free potassium cyanide. Even in that case it cannot be kept for any length of time. The freshly-prepared solution is at once decomposed by acids, turning green. It gives off a slight odour of hydrocyanic acid, as does the solid salt itself. The solution is at first stable toward alkalis in the cold, but on heating or standing for some time the hydroxide separates out.

The solution yields coloured precipitates with the neutral solutions of various metals, of which the following are the most distinct:—

Ferrous iron	Red-brown.
Cadmium..	Yellow.
Copper	Yellow.
Nickel	Purple.
Manganese	Greenish-yellow.

Silver and mercury salts are reduced by it, with deposition of the metals. None of these precipitates is stable toward acids, and their colour soon undergoes a change on standing.

We have made repeated attempts to isolate the purple precipitate which separates on the first addition of potassium cyanide to the vanadic solution, but without success. The compound, probably vanadic cyanide, is extremely unstable, and on drying yields a green or brown amorphous product, which is obviously a mixture.

The vanadicyanides of ammonium and sodium seem to exist only in solution. Vanadium cyanide dissolves in excess of ammonium cyanide or sodium cyanide, to solutions of the same colour as that of the potassium salt. No crystalline products, however, could be obtained from either solution, either by evaporation or precipitation with alcohol. When the latter is employed the compounds decompose at once, with separation of a thick blue paste.

The properties and reactions of potassium vanadicyanide are of special interest in view of the relative stability of the complex cyanides of the other metals of the group. The only stable compounds of trivalent cobalt are those which contain the metal as a constituent of a complex radical, either positive, as in the cobaltiamines, or negative, as in $K_3CO(CN)_6$, $H_3Co(CN)_6$, &c. The corresponding ferric compounds, *in comparison with other ferric salts*, are somewhat less stable than the cobaltic compounds as compared with simple cobaltic salts. Thus, for example, potassium ferricyanide is less stable, compared with ferric sulphate, than is potassium cobalticyanide when compared with cobaltic sulphate. The

* From the *American Chemical Journal*, xx., No. 7.

complex manganese derivatives are relatively still less stable. Among the latter is a sodium salt, $Na_3Mn(CN)_6$, but the free acid is unknown. Chromic cyanide yields neither an acid, $H_3Cr(CN)_6$, nor a sodium salt, and ammonium chromicyanide (*Ann. Chem., Liebig*, iii., 163) is very unstable. The chromicyanide solutions, however, are stable towards alkalis even on boiling. In the case of vanadium, neither the sodium nor ammonium salts can be obtained; potassium vanadicyanide is instantly decomposed by acids, with evolution of hydrocyanic acid, and is stable towards alkalis only in the cold. The simple vanadic salts are comparatively stable. Aluminium, which has the lowest atomic weight of all the metals in the group, is precipitated as hydroxide when potassium cyanide is added to its solution, and no cyanogen compounds at all of this metal can be obtained. The tendency to form complex radicals, throughout the entire group, as compared with the tendency to form simple salts, is thus seen steadily to diminish with a decrease in the atomic weights of its members.

Potassium Vanadisulphocyanate, $K_3V(CNS)_6\,4H_2O$.—Among the characteristic compounds of trivalent chromium the derivatives of chromic sulphocyanate are very prominent. Potassium chromisulphocyanate, $K_3Cr(CNS)_6.6H_2O$, is almost as stable as the chromicyanide. It is not decomposed by either alkalis or acids in cold solution (Rösler, *Ibid.*, cxli., 185). A number of other salts, such as $Ag_3Cr(CNS)_6$, $Ba_3[Cr(CNS)_6]_2$, &c., derivatives of the same acid, $H_3Cr(CNS)_6$, are also known.

We have succeeded in preparing a compound of vanadium analogous to this potassium salt, and find that it corresponds very closely to the latter in its reactions. The method employed was as follows:—

An alcoholic solution of potassium sulphocyanate was made by fusing sulphur with potassium cyanide (*Chem. Zeitung*, 1866, 666), digesting the product with absolute alcohol, and filtering. To this solution was added somewhat less than the calculated quantity of vanadium chloride, dissolved in a small volume of water. A precipitate of potassium chloride at once appeared, and the solution assumed a deep brown colour. After digestion for an hour on the water-bath the solution was concentrated by evaporation, and then placed in a vacuum-desiccator to crystallise. The first crop of crystals consisted of a mixture of about equal proportions of potassium sulphocyanate and vanadisulphocyanate. This was removed, and the evaporation continued until the solution was of a thick syrupy consistency. A large quantity of homogeneous, dark red crystals, almost black, were thus obtained. They were cleaned as thoroughly as possible by pressure between filter-paper, washed with ether, and dried in a vacuum. The analysis gave the following results:—

	Calculated for $K_3V(CNS_6).4H_2O$.	Found.
K	19·90	19·52
C	12·24	—
N	14·29	14·73
S	32 65	33·23
V	8·68	8·55, 8·22, 8·79
H_2O	12·24	13·09
	100·00	

Potassium vanadisulphocyanate, like the corresponding chromium salt, is extremely soluble in both alcohol and water, but is stable only in presence of an excess of potassium sulphocyanate. The pure salt is decomposed by either solvent, forming a green solution. Crystals mixed with a small quantity of sulphocyanate are very hygroscopic, dissolving in the water absorbed. Toward oxygen the salt is the most stable of any which we have prepared. The vanadium in the radical $V(CNS)_6$ undergoes oxidation only very slowly, and in presence of potassium sulphocyanate the solution may be left exposed to the air for some time without losing its characteristic dark brown colour. Alkalis precipitate vanadic hydroxide from the solution only on boiling, but it is at once decomposed by acids.

The preparation of corresponding salts of other metals, such as $Na_3V(CNS)_6$, $Ba_3[V(CNS)_6]_2$, &c., we have not yet attempted, but we hope to do so in the near future. Our investigations on the vanadic compounds in general will be continued.

ON THE

TRANSFORMATION OF CHEMICAL ENERGY INTO ELECTRIC ENERGY.*

By Prof. F. FOERSTER.

THE number of galvanic elements prepared and used for different purposes is very considerable. Several of them, such as the Daniell cell modified by Meidinger, have been extensively used for the production of small currents. But their adoption for the production of large currents would be too expensive, since they require and use up quantities of expensive material, such as zinc for example. On the other hand, all efforts to increase the electromotive force of galvanic cells have met with very little success, and we now know, thanks to the remarkable theory of Nernst, that the nature itself of these cells will not allow of the electromotive being raised to more than 2 or 3 volts. It is therefore necessary to find a substance as cheap as possible if we wish to produce commercially an electric current by means of a galvanic battery; carbon has long been thought of,—its potential energy already serves as the source of power in most industrial undertakings.

The problem of the oxidation of carbon or of its commercial compounds, in galvanic cells in the cold, so as to obtain its potential energy in the form of an electric current, has occupied the attention of electricians for more than twenty years, and has formed the subject of innumerable patents. The most interesting of the earlier researches on this subject were recently published in a review in the *Zeitschrift fur Electrochemie* (vol. iv., pp. 129 and 165). The great importance of this problem was demonsrated by Ostwald in 1894 in an address delivered before the general assembly of the German Electrochemical Society (*Zeit. f. Elect.*, i., pp. 81 and 122), and it still holds good up to the present. If we compare the number of electrochemical processes introduced commercially with the number of those which have been proposed, and which might have a certain value, we see that the first-named form has only an insignificant minority, and this is due more than anything to the high price of the electric energy. In places where hydraulic power is obtainable,—such as in the Alps, in Norway, Sweden, at Niagara, and latterly also on the Ebro, a river which has a very rapid current,—the electrochemical industry has commenced to develope, for under such conditions electric energy is comparatively cheap. But if we are obliged to produce the electric energy from coal, by burning it to form steam, and transforming the energy of the steam into mechanical energy, the final utilisation of the energy in the carbon is very incomplete. To begin with, the transformation of the heat of combustion of the coal into mechanical work by the aid of furnaces, boilers, and engines, gives a loss of 85 to 86 per cent of the total energy.

It is therefore clear that this return is much too expensive for a large number of chemical processes which, however, employ carbon directly. But it would be quite otherwise if we could transform the latent heat of the coal directly into electric energy by its combustion in the

* *Moniteur Scientifiquv*, Series 4, vol. xii., July, 1898.

cold in galvanic cells; under such circumstances we might be quite content to utilise only one-third, or even one-half, of the energy.

Since carbon in the state of coke or gas carbon is a good conductor of electricity, it appears rational at first sight to use it in one of these forms as the soluble electrode in the galvanic cell. A very simple element of this nature was made by M. Cochu (*Zeit. f. Elect.*, ii., p. 541). It is based on the well-known fact that carbon can be kept in solution by concentrated sulphuric acid, especially when hot. Cochu plunged the coke or gas carbon into sulphuric acid, using a plate of peroxide of lead as the source of oxygen. The cell, closed through a resistance of 100 ohms, possesses an electromotive force of 1·03 volts, and the current continues until the complete reduction of the peroxide of lead.

We have heard nothing further of this cell. To give it a practical value it would be necessary to replace the peroxide of lead by an electrode which would not be attacked, near which a current of air would play the oxidising part of the peroxide.

Jacques (*Zeit. f. Elect.*, ii., pp. 604 and 4130) attempted to make a carbon cell on another principle. He plunged the carbon into melted caustic soda contained in an iron crucible heated externally. Air was blown into the melted mass below the carbon. A current was established between the carbon and the iron in the interior of the cell. By using large external resistances an electromotive force of 1 volt could be obtained.

Nevertheless we can see that the Jacques cell does not affect the problem we have before us. In this case it would be necessary to direct the current of energy towards the iron and not towards the carbon, since the general principle of the construction of galvanic elements requires that the materials whose reaction serves as the source of electric energy should not mix, but remain separate one from the other: this is a condition necessary for the transformation of chemical into electrical energy. Thus the precipitation of salts of copper by zinc can only produce a current when the zinc is out of the solution of sulphate or other cupric salt. This is the case in the Daniell cell.

It is the same with several other processes,—for example, with those when the oxidation of the carbon is effected by the aid of a melted nitrate. It would be superfluous to mention them all in this article; and, further, I should not have described the cell made by Jacques if—thanks perhaps to the claims put forward—there had not been several interesting researches carried out on the subject, which have thrown a good deal of light on the nature of galvanic cells with melted electrolytes.

Andrews (*Zeit. f. Elect.*, iii., p. 117) and Reed (*Ibid.*, iii., p. 121) first thought that the Jacques cell constituted a species of thermoelectric element, since the iron is heated externally, while the carbon is cooled by the air. This opinion seemed to be confirmed by an experiment which showed that the electromotive force of the Jacques cell varied according to the difference of temperature of the two electrodes, and that the same phenomena could be reproduced when the carbon was replaced by certain metals. However, all the phenomena could only be produced irregularly, which led Andrews to suppose that the thermoelectric phenomena were here accompanied by electrochemical reactions. Latterly Liebenow and Strasser have succeeded in throwing light on these very remarkable reactions, and in showing that they constitute the principal source of the electromotive force in the Jacques cell (*Ibid.*, iii., p. 353). If we plunge rods of iron, nickel, or silver into melted potash, putting them in connection with a normal electrode, it will be seen that from the commencement they have a negative potential, and that the nickel dissolves in the potash with the evolution of hydrogen; but after some time a reaction followed by the absorption of heat suddenly takes place, and the potential between the metal and the electrolyte becomes 1 volt less negative than before; the oxygen of the air has oxidised the molten mass, and the metal is now passive. Carbon also dissolves in melted potash, giving off hydrogen; it, however, does not become passive, but keeps its potential, which is about the same as that of iron at the commencement of the reaction. Thus if we simultaneously plunge iron and carbon into melted potash through which the oxygen of the air has free passage, we obtain an electromotive force of 1 volt as soon as the iron has become passive. The air blown in first makes the iron passive, and then depolarises the carbon, driving off the disengaged hydrogen.

The Jacques cell works by consuming caustic potash, and consequently does not in any way affect the problem set above. Its electromotive force increases slightly with the rise of temperature; this partly explains the results found by Andrews and Reed.

If we examine the processes which require carbon as the soluble electrode more closely, we can easily see that they have no chance of effecting the complete solution of our problem. On the one hand, the ash from the carbon would soon interfere very considerably with the action of the cell, and, on the other hand, the carbon should be made a very good conductor of electricity, which is very difficult with certain kinds of carbon, and besides is always very expensive.

These difficulties have given rise to the idea of replacing the carbon in its natural state by certain gaseous products which can be obtained, notably by means of carbonic oxide, and perhaps also by hydrocarbides which would be brought into contact with the insoluble electrodes to burn them into carbonic acid. At first sight the choice of this method does not seem to be very advantageous, since the ordinary combustion of carbon to carbonic oxide is accompanied by a considerable loss of potential energy in the state of heat.

We know that the formation of a gramme-molecule of carbonic oxide by the combustion of carbon gives 29,000 calories, while the final oxidation of carbonic oxide into carbonic acid is accompanied by the disengagement of 68,000 calories. But the first part of the energy is in no way lost for the production of the electric current. We know that this energy represents exactly the heat necessary for effecting the decomposition of water by carbon, $H_2O+C=CO+H_2$, and which is consequently refound in the potential energy of the hydrogen and the carbonic oxide. That is precisely the basis of the commercial production of water-gas. In the last place it will be necesssary to bring this gas into the carbon cell. We shall see directly that the presence of hydrogen cannot be but advantageous.

As for the construction of such a cell, it must have the form of a gas element. This interesting type of galvanic element was discovered by Grove, who showed that two strips of platinum, charged electrolytically the one with hydrogen and the other with oxygen, plunged into dilute sulphuric acid, gave birth to an electric current which passes through the acid from the hydrogen to the oxygen. The phenomenon is produced far better if the two strips have been previously platinised by an electrolytic deposit.

In what now follows we must suppose the element of the Grove type of cell to be of the following form:—Two vertical glass tubes opened at the lower end and closed on the top, plunged into dilute sulphuric acid; two strips of platinised platinum are introduced, one in each; the tubes are charged, one with hydrogen and the other with oxygen. If now we connect the two strips by means of a wire, we find a current of 1·07 volts passing through the wire. At the same time the volume of both the gases diminishes, that of the hydrogen going twice as fast as that of the oxygen; the electric current ceases when the gas has completely disappeared.

This interesting phenomenon is explained in the following manner:—The oxygen by its solution in water tends to form negative ions O [according to Nernst (*Berichte*, xxx., p. 1555) the water will contain, besides

the ions OH, other ions O, and it is these latter that probably here play the principal *rôle*]. Perhaps a very small number of the atoms of oxygen to be found in the platinum become transformed into ions; but this transformation cannot take place without an equivalent quantity of positive electricity being spread over the platinum, and between this electricity and the negative charges of the oxygen ions there would be an attraction.

But this attraction would disappear if the positive electricity of the platinum could be otherwise directed. This is what takes place in our experiment:—The positive electricity of the platinum diffuses, by means of the wire, to the second platinum strip which is in contact with the hydrogen. This, on becoming charged with positive electricity, gives hydrogen ions, and it is thus that the two gases become transformed into ions of water and remain in the electrolyte,—that is to say, in the sulphuric acid. In this manner we find ourselves in the presence of a combustion of hydrogen in water, in the cold.

In a carbon cell the hydrogen ought to be accompanied or replaced by carbonic oxide, or perhaps by hydrocarbides. The sulphuric acid ought to give place to another electrolyte which would allow these carbon compounds to change into positive ions, and to combine with the oxygen ions, giving water or carbonic acid.

(To be continued).

A TABLE OF ATOMIC WEIGHTS.*

By THEODORE WILLIAM RICHARDS.

Since no natural constants are more used by chemists than the atomic weights, it is a matter of great importance for every one, from the chemical philosopher to the practical analyst, to have a convenient table of them always at hand. Unfortunately the present state of our science makes the selection of the values often a matter of personal opinion; and because this is the case, it is well that many of those who have had experience in accurate quantitative analysis should express their views. Hence arose the present work, which was begun solely for use in Harvard College.

It is true that an accurate table of atomic weights may sometimes be less appropriate for the calculation of analyses than an inaccurate one, for the constant errors of any one process are eliminated as much as possible from the accurate table, and, moreover, all the results are reduced to the vacuum standard. Of course neither of these refinements is to be expected in common work, although many uncorrected methods may yield results which are very consistent among themselves. Obviously the best table for the practical calculation of analyses would be a list of factors, in which each quantity had been found empirically according to precisely the method which is to be employed in the analysis of an unknown substance (compare Seubert, *Ber. d. Chem. Ges.*, xxi., 2180). Since, however, the errors of ordinary work often eliminate one another, and, since such a table of empirical factors would have to be accompanied by exceedingly minute directions, the scientifically accurate table of atomic weights is generally the most convenient substitute for the factors demanded by the analyst, as well as the most suitable basis for theoretical considerations concerning the periodic system of the element.

In the compilation of the accompanying table the chief emphasis has been laid on the probable chemical accuracy of the processes involved in each case. The search for possible causes of constant chemical error has usually furnished the evidence, if any evidence was to be obtained, upon which has been based the sometimes very puzzling decisions between conflicting data. For example, the possible occlusion of foreign matters by many precipitates has always been borne in mind, as well as the fact that crystals obtained from aqueous solutions usually retain with great obstinacy important amounts of mother-liquor enclosed within their structure. Oxides and other substances obtained by ignition often have a tendency to occlude traces of other materials remaining from their mother compound; of course the possibilities of such a serious error must be carefully weighed in each case. Most experimenters upon the volumetric ratio of silver to the chlorides have produced erroneous data, through lack of knowledge of the dangers of this apparently simple process. These results must then be given small weight, no matter how concordant they may seem. The solubility of glass and porcelain, as well as nearly all precipitates, is another frequently overlooked source of grave complications, and so is the action of many substances upon their containing vessels at high temperatures. The fact that in some cases the necessary methods of calculation greatly magnify the experimental error was not forgotten. These and many other equally obvious minor principles have served as the guides in the selection of the figures below; but of course the results cannot be considered ultimate. "Post-mortem examinations are often unable to detect the more subtle poisons." In many cases much more experimental work is needed, not only to secure new data, but also to show where the old are in error. While, however, it is very important to show such falsity, the attempt to counteract it numerically by the application of small corrections is a dangerous remedy; for minor conditions often seriously modify the minor corrections. In such cases wholly new data must usually be obtained, and these must be corrected, if correction is necessary, by him who is familiar with every step of the processes involved.

One is continually reminded, as he studies the conflicting evidence of the words of Ostwald:—"Differenzen sind nicht selten, und mahnen ernstlich an die Unvollkommenheit menschlicher Arbeit, aber auch an die Verantwortung welcher jeder übernimmt, welcher einen numerischen Wert der Oeffentlichkeit mitteilt" (*Ztschr. Phys. Chem.*, iii., 143). This responsibility is not always realised by eager investigators, who seek to make up for a possible lack of quality by a superabundance of quantity. "A single determination, well worked out, is better than twenty incomplete ones. Too much cannot be said against the multiplication of incomplete or carelessly obtained data; for such data carry with them not only uncertainty and confusion in the present, but also additional labour for a reviser in the future" (*Proceedings Amer. Acad.*, xxxi., 99; xxvi., 294). Every reaction must be assumed to involve some constant error, and every substance must be assumed to contain some constant impurity, until a proof of the contrary is obtained. Our wofully discordant data furnish a heavy presumption against almost any chemical method, when greater accuracy than one part in four or five hundred is desired.

The standard O = 16·000 is adopted below, as likely to be the most convenient for many years to come (compare F. W. Küster, *Ztschr. Anorg. Chem.*, xiv., 251). The last figure of each number given in the following table cannot be considered in any case certain. It is often probably not much more than one unit in error, although the uncertainty may amount to as much as six or eight units in some cases. Of course the decimal notation does not admit of closer indications without an individual explanation in each case. For example:—Iron, germanium, and gallium are given in the table as 56·0, 70·0, and 72·5 respectively. The first is probably known within 0·1 or 0·2, while the other two may easily be 0·5 in error; but the method of expressing the results does not admit of this grade of distinction.

The aim has been to construct a convenient working table, which shall carry with it all that is trustworthy, and nothing that is unnecessary. It is almost needless to state that the well-known standard works of Clarke, Meyer and Seubert, Ostwald, Van der Plaats, and others,

* Presented to the American Academy of Arts and Sciences, March 9, 1898. From the *American Chemical Journal*, xx., No. 7.

have been freely consulted in the preparation of this table, as well as many of the original papers.

Especially am I indebted to Professor Clarke for his latest gigantic collection of data and results (Smithson, "Misc. Coll. Constants of Nature," v., 1897), which would have made the present table a work of supererogation, if he had viewed the subject from a somewhat less mathematical standpoint. Professor Clarke's method of decision places the credit with the skilful manipulator; I have striven to give the thoughtful chemist who is not so clever with his hands the credit which I think belongs to him. The fact that the two tables usually agree is due either to the best methods having fallen into the best hands; or to Professor Clarke's having wisely forsaken the rigid application of his principle; or else, especially in the case of the rare metals, to the lack of data affording room for intelligent difference of opinion. Among the seventy-four atomic weights given in the table, only seven differ enough from the values computed by Clarke to excite remark. It seems fitting to give a brief statement of the reasons for the differences in those seven cases, leaving the details of reasoning about the other sixty-seven elements unpublished. The elements mentioned are antimony, cadmium, calcium, magnesium, platinum, tungsten, and uranium.

It is not my purpose to enter at length into the discussion of the antimony problem. Much of the voluminous work upon this subject is now rejected by common consent. The work of Bongartz (*Ber. Chem. Ges.*, xvi., 1942, 1883), sometimes accepted as the best because it is the most recent, has the grave faults inherent in all methods which involve the precipitation of baric sulphate. Among all the published data Cooke's analyses of antimonious bromide (*Proc. Am. Acad.*, v., 13, 1877), Sb=119·92, seem to me the most satisfactory, because of the admirable fitness of argentic bromide for quantitative work, and because of the many precations used in both preparation and analysis. Cooke's and Schneider's (*Pogg. Ann.*, xcviii., 293, 1856; *Jour. Prakt. Chem.*, [2], xxii., 131, 1880) work upon the sulphide, Sb=120·5, are perhaps the next in order; but Cooke's work upon this subject was far less satisfactory than his work on the bromide. Accordingly the value 120·0 is given as the atomic weight of antimony in the accompanying table, instead of 120·43, computed by Clarke.

Although the atomic weight of cadmium has been the subject of many investigations, it is still far from certainly established. Many reasons combine to make me think that the highest of the published values are the most accurate. Dumas's (*Ann. Chem., Liebig*, cxiii., 27, 1860) work upon the chloride of cadmium led to the value 112·23; but his method of investigating chlorides sometimes gave him too low results (see *Proc. Am. Acad.*, xxx., 371; cases in point—barium, strontium, sodium, and tin). V. Hauer (*Jour. Prakt. Chem.*, lxxii., 350, 1857) and Partridge (*Am. Jour. Sci.* [3], xl., 377, 1890) found cadmium equal to less than 112 by heating cadmic sulphate in a stream of hydric sulphide, but there is no proof that their initial substance was thoroughly dried. On the other hand, Bucher's conversion of cadmic sulphate into the oxide led to the value 112·36, which Bucher regards as the minimum ("Johns Hopkins Inaug. Dissertation, Baltimore, 1892"). This method is one in which the tendency of the oxide to retain sulphuric acid is approximately neutralised by the tendency of the sulphate to retain water: this fact is demonstrated by Baubigny's (*Comptes Rend.*, xcvii., 906, 951, 1369; 1883) good results on zinc, nickel, and aluminium, as well as Marignac's (see under Magnesium, later in this paper; compare *Proc. Am. Acad.*, xxvi., 260, 273; xxxi., 160) on magnesium. The results of Lenssen (*Jour. Prakt. Chem.*, lxxix., 281, 1860), Partridge, Morse and Jones (*Amer. Chem. Journ.*, xiv., 260), and Bucher, involving the use of cadmic oxalate, all in the neighbourhood of 112, are likely to be too low because of the great difficulty of freeing this substance from water. Morse and Jones have clearly indicated this and other possible causes of error. Moreover, I doubt very much if it is possible to prepare the oxalate free from the nitrate by precipitation from solutions containing cadmic nitrate. The method of calculation magnifies either error by introducing it in opposite directions into the numerator and denominator. Bucher's extended work casts grave doubts upon cadmic oxide (used by Morse and Jones, and Lorimer and Smith) (*Ztschr. Anorg. Chem.*, i. 364) as a suitable substance to serve for a basis of operations. On the other hand, the work of Huntington (*Proc. Am. Acad.*, 1881, p. 28) and Bucher with a bromide (a very satisfactory substance as to its preparation because it may be sublimed, and as to its analysis because of the insolubility of argentic bromide), and that of Bucher with calmic chloride, point toward 112·3 or 112·4 as the probable figure. The electrolytic work of Hardin (*Journ. Am. Chem. Soc.*, 1896, xviii., 1016) upon these compounds, performed unfortunately with small amounts of material, is nevertheless in favour of the lower value, 112·0, so that any value adopted must be uncertain. Clarke computes 111·95; for the accompanying table 112·3 has been chosen.

There is good reason for believing that Clarke's value for calcium (40·07) is probably too high. The only determinations worth considering are those of Erdmann and Marchand upon the composition of Iceland spar, and only one out of their thirteen experiments is corrected for known causes of constant error (*Journ. Prakt. Chem.*, xxx., 257, 1850). This experiment, which really constitutes the sum and substance of our pseudo-accurate knowledge of a very important quantity, makes calcium almost exactly 40·0. Obviously but little confidence may be placed in such meagre material; it is surprising enough that so common an element has remained forty years untouched on so unsatisfactory a basis. An extended investigation, now well advanced in this laboratory, has as its object the securing of less impeachable data upon the atomic weight of this frequently appearing constituent of the universe.

Marignac's results (*Arch. Sci. Phys. et Nat.*, [3], x., 206) from the quantitative ignition and synthesis of magnesic sulphate, processes in which the constant errors are likely to eliminate one another, have been so completely confirmed by the recent work of Richards and Parker (*Proc. Am. Acad.*, xxxii., 53; *Ztschr. Anorg. Chem.*, xiii., 81, 1896) that magnesium is represented by the figure 24·36 in the table. The results of the syntheses of magnesic oxide by Burton and Vorce (*Amer. Chem. Journ.*, xii., 219, 1890) have been shown by Richards and Rogers (*Proc. Am. Acad.*, xxviii., 200) to be under the cloud of a serious possible constant error, and no other results offer weighty evidence against the value just named.

(To be continued).

Preventive of Rust on Metal Work.—Lard 125, camphor 20, are melted together and a little graphite added. The objects are dressed with this paste, which is removed after twenty-four hours.

Banquet to Past Presidents of the Chemical Society.—The banquet of the Chemical Society to those of its Past Presidents who have completed fifty years' Fellowship of the Society, which was postponed last June owing to the lamented death of the Senior Past President, Lord Playfair, is now arranged to take place on Friday, November 11, at the Hotel Métropole. The Past Presidents who will then be entertained are:—Sir J. H. Gilbert, F.R.S.; Sir Edward Frankland, F.R.S.; Professor Odling, F.R.S.; Sir F. A. Abel, Bart., F.R.S.; Dr. A. W. Williamson, F.R.S.; and Dr. J. H. Gladstone F.R.S.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 24, June 13, 1898.

Spectral Researches on the Atmospheric Air.—H. Moissan and H. Deslandres.—Already inserted.

On the Mixture of Gases.—D. Berthelot.—The author reviews the results obtained by previous workers on the subject, such as Dalton, Amagat, Sarrau, Leduc, &c., with regard to the densities and pressures of gaseous mixtures. He goes on to show in a long mathematical paper that previous theories are not tenable, but that the one he has developed is the only one which will in every case agree with experiment.

Atomic Weight of Nitrogen.—M. Vèzes.—The comparison of the atomic weights, calculated according to the method given by M. Berthelot, with the atomic weights found by chemical analysis gives a very satisfactory concordance for certain elements (hydrogen, carbon), while with certain other elements (chlorine, sulphur, phosphorus, and above all nitrogen) it shows a considerable divergence. Taking the atomic weight of oxygen as 16·000, we get for hydrogen, from the physical observations of M. Berthelot, 14·005, and by chemical analysis (Stas) 14·044. The divergence between these two numbers is, as can be seen, nearly three-thousandths of their value. Berthelot explains this difference by a systematic error which vitiated the results of the classic work of Stas. This error was first pointed out by Dumas, who showed that the granulated silver used by Stas retained a certain amount of oxygen which was dissolved during its fusion. But this point was answered by Stas in a paper published after his death, and according to his calculations the atomic weight of nitrogen would be—

Stas	14·044
Corrected value	14·040

The systematic error pointed out by Dumas does not, therefore, hold good.

Atomic Weight of Tellurium.—R. Metzner.—The determination of the atomic weight of tellurium has been the subject of numerous researches. The latest results give figures comprised between 127·05 and 127·74. The author's experiments were carried out according to the two methods which appeared to be the most to be relied upon. First, the use of sulphate of tellurium, and, secondly, the reduction of tellurous acid; the results of all the experiments have given him numbers higher than those of Brauner and Staudenmaier, the mean of his results being 127·9.

Action of Sodammonium in excess on Red Phosphorus.—C. Hugot.—The results of the action of phosphorus in excess on sodammonium has already been published (*Comptes Rendus*, cxxi., p. 206). The action of sodammonium in excess on phosphorus gives rise to a compound which is fully described in this paper. A yellow body is formed corresponding to the formula $P_2H_3Na_3$; this yellow body treated by acids and water gives rise to the following reactions:—

$$P_2H_3Na_3+3HCl=3NaCl+2PH_3$$

and

$$P_2H_3Na_3+3H_2O=3NaHO+2PH_3.$$

Heated in vacuo the body $P_2H_3Na_3$, after having lost the little ammonia gas it contains, gives off at about 100° phosphide of hydrogen and a little hydrogen; on increasing the heat the proportion of these two gases given off changes, until at 200° to 300° nothing but hydrogen is collected.

Preparation and Properties of a New Carbide of Tungsten.—P. Williams.—Already inserted in full.

New Method for the Separation of Geraniol and Citronellol.—J. Flatau and H. Labbé.—The authors describe how they have prepared a certain quantity of ethers from the two alcohols. The product obtained is washed very carefully with carbonate of soda, and then fractionated in vacuo. After several distillations the ethers are precipitated from the alcohols in excess; by titration 98 per cent of pure ether is found. Both these ethers possess a very agreeable odour.

MISCELLANEOUS.

Glasgow and West of Scotland Technical College.—*Prize of £30 and Research Studentship in Chemistry.*—The Directors of Nobel's Explosives Company, Limited, after consultation with Dr. G. G. Henderson, Freeland Professor of Chemistry in the above College, have decided to give a prize tenable under the following conditions:—

(1). The prize to be £30, and to be known as the "Nobel Company Prize."

(2). The prize to be awarded annually, until further notice, to a student in the chemical laboratory of the Technical College who has passed through the usual course of training in that laboratory, and who, in the opinion of the Professor of Chemistry for the time being, is qualified to prosecute research.

(3). The holder of the prize to engage in research work in the chemical laboratory of the Technical College, under the direction of the Professor of Chemistry for the time being, for the period of one academical year, viz., from beginning of October until middle of July.

(4). The prize to be awarded by the Professor of Chemistry for the time being, but to be withheld in any year if there is at that time, in his opinion, no student in the chemical laboratory with the necessary qualifications.

It was also suggested by the Directors "that, while not making it a condition of the gift, the prize might be awarded by preference to a student who would be willing to accept it on the understanding that the Company would have the first call on his services, on terms not less favourable than those he might secure elsewhere." In accepting the gift on the above terms the Governors of the College further resolved to grant a free studentship for one year in the laboratory to the Nobel Company's Prizeman, thus raising the money value of the prize to about £50. The example of Nobel's Company might profitably be followed by other chemical manufacturers.

BOROUGH POLYTECHNIC INSTITUTE.

(Close to the OBELISK, ST. GEORGE'S CIRCUS).

The following EVENING CLASSES in CHEMISTRY (Lectures and Laboratory Work), under the direction of F. MOLLWO PERKIN, Ph.D., commence MONDAY, SEPTEMBER 26th, 1898:—

Elementary Course—Lectures, Fridays, 7.15—8.30; Practical Work, Tuesdays and Fridays, 7.30—10. Advanced Course, Lectures, Wednesdays, 7.15—8 30; Practical Work, Mondays and Wednesdays, 7.30—10. Elementary Organic Course—Lectures, Tuesdays, 7.35—8.30. Special Course, Tuesdays and Fridays, 7.30—10.

Fees for the Session either Course—Lectures: Members, 3s.; Non-Members, 5s. Practical Work: Members, 8s.; Non-Members, 10s.

Members taking Practical Work will be admitted free to the Lectures. Apparatus and Chemicals are supplied free in above classes, but a deposit of 5s. is charged to cover breakages.

Prospectus of the Institute, and Handbills of General, Commercial, Art, and Science Classes, and of Trade Classes, may be had on application.

C. T. MILLIS, Principal,
Education Department.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2029.

DALTON'S LAW.*

By W. N. SHAW, F.R.S.

Discrepancies between the sum of the partial pressures of air or nitrogen and saturated vapour and the pressure of mixtures of the gases respectively with saturated vapour, indicating *prima facie* a departure from Dalton's law, were shown by Regnault (*Ann. de Chim.*, [3], vol. xv.) to exist for water vapour: the extent of the difference being on the average nearly half a millimetre.

Regnault himself, in his classical paper on the Pressure of Vapours (*Mem. de l'Institut*, vol. xxvi.) sought to throw additional light on these discrepancies by examining the increase of pressure produced by adding ether or some other volatile liquid to an atmosphere, the pressure of which had been previously measured. In the course of these experiments, he concluded that he had satisfactorily ascertained the cause of the phenomena to be the condensation of the vapour on the vertical sides of the containing tube under a pressure of vapour less than the saturation pressure corresponding to the temperature. He regarded Dalton's law as being true, in fact, for a gas-filled space completely surrounded by a sufficiently thick layer of the evaporating liquid. In a vessel with solid vertical walls gravity prevents the formation of a layer of the required thickness on the vertical sides. This hypothesis was held to account for the fact that, if the mixture were compressed as in a Boyle's law tube, the pressure gradually diminished after the initial compression to a value less than that required by Dalton's law; in the case of ether about 10 m.m. of pressure were missing on this account.

Such a hypothesis would give a satisfactory explanation of the phenomena if the sides of the glass vessel were gradually dissolved away by the liquid condensing, as, for example, would be the case if the tube were made of rock salt, but if the action between the glass sides and the vapour were merely a mechanical one, the supposed continuous evaporation of liquid from the horizontal surface and its return to the stock by condensation on the vertical sides, and running down these, would seem to contradict the principle of conservation of energy.

Regnault's explanation is the more difficult to accept if the density of the vapour be considered. Prof. J. J. Thomson, in his "Application of Dynamics to Physics and Chemistry," has shown that the addition of air-pressure upon a liquid surface in contact with its saturated vapour ought to result in a slight additional evaporation, causing a slightly increased density of vapour, and the experiments of the author upon air at various degrees of saturation (*Phil. Trans.*, 1888) indicated some slight increase of density beyond that required to correspond with the vacuum pressure, so that any departure from Dalton's law could not be attributed to the want of mass of vapour in the saturated air.

The point might be investigated by examining closely the behaviour of a mixture of air and vapour under isothermal conditions in the neighbourhood of the point at which condensation begins to occur. At great rarefaction the mixture would behave as a perfect gas, and if the isothermal relation between p and $1/v$ were plotted on a diagram (with a suitable correction if necessary for the deviation of the air from Boyle's law) the curve obtained would be a straight line through the origin represented by $p = k \times 1/v$. At great concentration, if Dalton's law were strictly true, the relation would again be represented by a straight line, viz., $p = k' \, 1/v + p_v$; where k' is the Boyle's law constant for the contained dry air, and p_v is the saturation pressure of the vapour. This line would cut the vertical line $1/v = 0$ in the point distant p_v (*i.e.*, the theoretical saturation pressure) from the origin, and it would cut the line $p = 0$ in the point $1/v = -\frac{p_v}{k'}$. These two theoretical lines would meet if produced at an obtuse angle in the theoretical saturation point.

If, on the other hand, at the greater concentrations there were a discrepancy from Dalton's law proportional to the total pressure and therefore represented by the relation $p = k \times 1/v + p_v - \lambda p$, the observations would still show a straight line not quite coinciding in direction with the theoretical line for Dalton's law, but cutting that line in the point on the horizontal axis $(-p_v/k', 0)$, and cutting the vertical axis at a point distant $p_v/(1+\lambda)$ from the origin. Various other hypothetical laws of variation might also be suggested.

A series of observations thus plotted would enable one to determine whether the actual behaviour tended to approach agreement with Dalton's law, or some recognisable modification of it, such as that suggested.

Regnault's observations, recorded in the paper referred to, include a series of determinations of the pressure and related volumes of mixtures of air and ether vapour for the temperature 7·7° C. They also show the dry air pressures for the series of observed volumes, so that the pressure of this mixture can be plotted against the pressure of dry air for the same volume, and the correction for any deviation from Boyle's law for dry air is thereby made automatically. A diagram showing two sets of his observations was exhibited. The pressures ranged between 600 and 1400 m.m. It was pointed out that, for the observations at greater rarefactions, the theoretical line was very strictly adhered to until the pressure reached 80 per cent of saturation, then slight discrepancy in the direction of loss of pressure was indicated, increasing until it amounted to more than 10 m.m. for the theoretical saturation point; beyond that the discrepancy showed a slightly diminishing value. A straight line drawn to show a theoretical defect from Dalton's law amounting to λp (where $\lambda = 0{\cdot}007$) agreed much more satisfactorily with the plotted observations.

The second series of observations, made with a greater amount of ether, showed the discrepancy from Dalton's gradually vanishing with increasing pressure.

It was also pointed out that in drawing his conclusions Regnault had not taken account of the supersaturation of air which would result from compressing air at constant temperature in the absence of nuclei for condensation, and the time that would be required under these circumstances for the gradual deposition of the excess of moisture upon the liquid surface exposed to it.

Moreover, it seems most unlikely that if the presence of air caused a discrepancy of 10 m.m. for a total pressure of 1000 m.m., the increase of the air pressure to 1400 m.m. should do away with the discrepancy previously caused. In other words, the line connecting the observations and intersecting the theoretical Dalton's law line at the highest pressure recorded is antecedently improbable and unreal.

It may therefore be concluded that Regnault's explanation is probably an unreal one, and that an actual divergence from Dalton's law is indicated. The amount of the divergence, however, cannot be finally deduced from the records of Regnault's observations, and must await a repetition of those or similar experiments in which the errors which may be due to supersaturation are guarded against.

* A Paper read before the British Association (Section A), Bristol Meeting, 1898.

Appointment.—Mr. W. Lincolne Sutton has been appointed Public Analyst for East and West Suffolk, Ipswich, and Bury St. Edmunds, in succession to the late Mr. J. Napier.

THE ACTION OF LIVING STRUCTURES ON THE PHOTOGRAPHIC PLATE.*

By PERCY FRANKLAND, Ph.D., F.R.S.

THE action exerted by uranium and its compounds, by zinc, and many metals, as well as by a number of organic substances, on photographic plates which has been revealed by the investigations of Becquerel, Colson, and especially of Russell, naturally leads to the enquiry as to whether *living* structures may not also be endowed with the power of recording their presence on the sensitive film of the photographer.

In commencing the study of this subject it has occurred to me that the group of the bacteria are perhaps of all organisms the best adapted for experiment in this direction, and I should like to take this opportunity of making known some of the preliminary observations which I have made.

Experiments A.

Gelatin dish cultivations of the well-known bacteria *Proteus vulgaris* and the *Bacillus coli communis* were used, the colonies being in each case densely packed. A sensitive plate (Imperial Flash-light) was placed on the top of the open dish, sensitive side towards the cultivation, another sensitive plate being placed beneath the dish containing the cultivation. Sensitive plates were similarly disposed above and below a similar dish containing the sterile gelatin culture medium. All the dishes and plates thus arranged were kept in a tin box in the dark room from June 11th to 20th, 1898, when they were developed with Imperial Standard Developer, and gave rise to the following effects:—

Proteus vulgaris	Top plate	Strong light effect.
	Bottom plate	No light effect.
B. coli communis	Top plate	Very strong light effect.
	Bottom plate	No light effect.
Blank gelatin dish	Top plate	No light effect.
	Bottom plate	No light effect.

The above results show that the bacterial cultures in question are capable of exerting an influence on the photographic plate at a distance of about half an inch, that this influence does not penetrate glass, and that the sterile gelatin medium does not affect the photographic plate.

The gelatin had only been inoculated with the bacteria in question on June 10th, so that the whole of the growth took place in the dark. The *Proteus vulgaris* liquefies the gelatin in about twenty-four hours, so that during the greater part of the nine days' exposure the medium must have been liquid. The *B. coli communis*, of course, does not liquefy gelatin.

Experiments B.

In the next instance I tried whether definite pictures of bacterial colonies could be obtained by placing the sensitive film in direct contact with the growths. For this purpose Austin Edwards's double instantaneous Frena films were employed, and cut so that they could be dropped sensitive side downwards into the dish containing the culture.

This was first done with a gelatin dish containing two large colonies which had grown from bacteria which had accidentally gained access from the air.

The colonies had been growing from June 4 to 24, and the Frena film was exposed to their action from June 24 to 30, 1898. On then developing with Imperial Standard Developer, distinct images of the colonies made their appearance, and were of sufficient density to yield a feeble print.

Better results were obtained with a cultivation of the *B. coli communis* consisting of large colonies. The cultivation was started on June 22, 1898, and the sensitive film exposed to it from July 1 to 14, 1898. On developing, very distinct images of the colonies were obtained, and sufficiently dense to print fairly well.

An exactly similar experiment made with the typhoid bacillus yielded a feebler result.

Experiments C.

As is well known, the growths of some bacteria are luminous in the dark. An agar-agar culture of the *Photobacterium phosphorescens* exhibiting a number of phosphorescent colonies, which had been growing from July 7 to 19, 1898, was placed in contact with the sensitive film from July 19 to 28, 1898. On development, very strong images of the colonies were obtained, and of much greater density than in the case of the non-phosphorescent bacteria with which I had previously experimented.*

Experiments D.

Much thicker growths are generally obtained by what is known as "streak culture," and it was thought that with such streak cultures probably stronger effects on the photographic plate would be obtained. This anticipation was fully realised in the case of a streak culture of *Proteus vulgaris* on agar-agar which had been growing from July 7 to 19, and was placed in contact with the Frena film from July 19 to 28, 1898. This yielded a very strong picture on development.

These preliminary experiments enable the following conclusions to be drawn:—

1. That ordinary bacterial cultures on gelatin and agar-agar are capable of affecting the photographic film, even at a distance of half an inch, whilst, when placed in contact with the film, definite pictures of the bacterial growths can be obtained.

2. As this action does not take place through glass, it is in all probability due to the evolution of volatile chemical substances which enter into reaction with the sensitive film, and I think it will be found to be analogous to the phenomena observed by Dr. Russell in the case of some organic compounds.

3. As far as my experiments have gone, the action is exerted both by bacteria which liquefy (*Proteus vulgaris*) and which do not liquefy gelatin (*B. coli communis* and typhoid bacillus). It is, however, quite possible that considerable differences, as regards activity towards a photographic plate, may be found to exist in the case of different bacteria, and that this property may become of importance in their diagnosis.

4. Bacterial growths which are luminous in the dark (*e.g.*, *Photobacterium phosphorescens*) exert a much more powerful action on the photographic plate than the non-luminous bacteria with which I have hitherto experimented. In the case of these phosphorescent bacteria, the action on the photographic film is not perceptibly diminished by the interposition of a glass plate.

The experiments of which I have given some account are, of course, of an entirely preliminary character. Further experience will doubtless lead to improvement in the photographic effects obtained, and I propose extending these investigations, not only in connection with bacteria, but also in respect to other organised structures, vegetable and animal, living and dead.

I have pleasure in acknowledging the zealous help I have received in the photographic part of these experiments from my assistant, Dr. Turnbull.

Rhodin Patent.—The Appeal against Mr. Justice Bigham's judgment in the Castner Kellner action is likely to be reached by the end of next month, when the validity of the Rhodin Patent will again be fully considered.

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* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

* I have since found that the influence of phosphorescent bacteria on the photographic film is capable of readily traversing glass.—October 1, 1898.

THE OXIDATION OF GLYCEROL IN PRESENCE OF FERROUS IRON.*

(Preliminary Notice).

By HENRY J. HORSTMAN FENTON, M.A., and HENRY JACKSON, B.A., B.Sc.(Lond.).

It has previously been shown by one of the authors (*Trans. Chem. Soc.*, 1894; *B. A. Report* 1895, &c.) that the presence of a small quantity of *ferrous iron* exerts a specific influence on the oxidation of tartaric acid. One molecule of the acid loses two atoms of hydrogen, and the result is hydroxymaleic acid, $C_2(OH)_2(COOH)_2$. Hydrogen dioxide is the most efficient oxidising agent for the purpose, but a similar result may be brought about by atmospheric oxygen in presence of sunlight, or by chlorine, bromine, &c. The presence of ferrous iron is absolutely essential, but the proportion necessary bears little, if any, relation to the yield of the product.

Similar effects appear to be produced by certain other hydroxy-acids (*Proc. Chem. Soc.*, 1898, 119), and the results of these are under investigation.

Messrs. Cross, Bevan, and Claude Smith have subsequently undertaken the investigation of the behaviour of *carbohydrates* when oxidised under similar conditions, and some of their results have already been published (*Trans. Chem. Soc.*, 1898), and Dr. Morrell is making important observations in the same direction.

With the object of extending the investigation of this reaction to other classes of hydroxy-compounds, the present authors are engaged in a study of the behaviour of certain *polyhydric alcohols* when similarly treated with oxidising agents in presence of iron. The first of these substances which has been selected is *glycerol*, and in this case again the presence of ferrous iron is found to exert a remarkable influence, as will be evident from the following observations:—

When a solution of glycerol (1 mol.) is mixed gradually with strong (20 volume) hydrogen dioxide (1 mol.), at the ordinary temperature, little, if any, change takes place. No alteration of temperature occurs, and the mixture, even after it has stood for some days, gives very strong reactions of hydrogen dioxide. Fehling's solution, in the cold, is unaffected, and the addition of phenyl-hydrazine acetate merely gives rise to an evolution of gas, owing to the presence of hydrogen dioxide, with slight precipitation of resinous matter. But when an exactly parallel experiment is made with the previous addition of a very small quantity of ferrous sulphate, a very powerful action results. The peroxide is now consumed almost immediately and the liquid becomes hot—the temperature, in fact, rises nearly to the boiling-point if the peroxide is added quickly. The resulting solution now strongly reduces Fehling's solution in the cold, and, when mixed with phenyl-hydrazine acetate at the ordinary temperature, a bulky yellowish-brown precipitate begins to separate almost immediately, and continues to do so for several days.

The substance thus precipitated crystallises from hot benzene in beautiful transparent golden prisms, which melt at 130°—131° (uncorr.), and is found by analysis to have the composition $C_{15}H_{16}N_4O$. It is, in fact, identical with *glycerosazone*, which has been obtained by Fischer and Tafel from "glycerose," by Piloty and Ruff from dihydroxy-acetoxime, and by Piloty from dihydroxy-acetone.

The oxidation-product obtained in the manner above stated may therefore be dihydroxy-acetone, glyceraldehyde, or, like Fischer's "glycerose," a mixture of both.

This product is now being investigated, and the authors also intend to make similar experiments with erythritol, mannitol, and other polyhydric alcohols.

* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

THE ACTION OF CERTAIN SUBSTANCES ON THE UNDEVELOPED PHOTOGRAPHIC IMAGE.*

By C. H. BOTHAMLEY, F.I.C., F.C.S.

It has been known for some time to practical photographers that just as there are substances that, like printer's ink, produce developable images when allowed to remain in contact with photographic plates, so there are others that under similar conditions will destroy a developable image previously produced on a photographic plate by the action of light. The author described one case in which printers' ink, acting through three or four thicknesses of tissue paper, destroyed the image previously produced by light; and others, in which the image was partially destroyed by exhalations from the material forming the hinges of double dark slides in which the plate had been kept for some time after being exposed.

Abney showed, many years ago, that the developable image is destroyed by the action of a solution of hydrogen peroxide, and the author finds that this effect is produced by the vapour as well as by the liquid. It is well known that hydrogen peroxide is produced during the oxidation of many substances; and these two facts together suggested the conclusion that the destruction of the photographic image, in cases such as those described, is really due to hydrogen peroxide. It was found that the vapour of turpentine, and other substances that are known to yield relatively large quantities of hydrogen peroxide during their oxidation by air, are particularly active in destroying the developable image produced by light.

The results are exactly the opposite of those described by Russell, and the author confirms Russell's observation that hydrogen peroxide vapour itself is capable of producing a developable image in a short time. The facts indicate that when hydrogen peroxide or substances that produce hydrogen peroxide during their oxidation by air, act on photographic plates in small quantity, or for a short time, they produce a developable image; but when allowed to act in larger quantity, or for a much longer time, they produce the opposite effect, and destroy the image already produced by light. In some cases it was found that in the early stages of the reaction the reducing effect of the substance was added to the effect of light, but on prolonging the action both effects were destroyed.

The observations are being continued.

* Abstract of a Paper read before the British Association (Section B), Bristol Meeting, 1898.

THE TEACHING OF SCIENCE IN ELEMENTARY SCHOOLS.†

The Committee are able to report that the quantity, if not the quality, of the teaching of science subjects in elementary schools has made progress during the past year. Table A, made up from the return issued by the Education Department, gives the figures for the scientific class subjects as compared with English. In the report for last year it was mentioned that the number of school departments taking object lessons would greatly increase, as the Government code of regulations announced that they would become obligatory in the three lower standards on and after September 1, 1896. We now see the result, so far as the schools are concerned whose school year ended between August 31, 1896, and August 31, 1897, but

† Report of the Committee, consisting of Dr. J. H. Gladstone (Chairman), Professor H. E. Armstrong (Secretary), Professor W. R. Dunstan, Mr. George Gladstone, Sir John Lubbock, Sir Philip Magnus, Sir H. E. Roscoe, and Professor S. P. Thompson. Read before the British Association (Section B), Bristol Meeting, 1898.

the full effect cannot appear until the next year's return, the whole of which will be within the obligatory period.

The number of departments in "schools for older scholars" for 1896-97 was 23,080, all but ten of which took one or more class subjects. But History was taken in 5133 departments, and needlework (as a class subject for girls) in 7397 departments, and sundry minor subjects in 1056, making, with the other four subjects of the table, a total of 55,456, This shows an average of more than 2¼ class subjects to each department; but it must be borne in mind that the same subject is not always taken in all the standards, in which case three class subjects will appear in the return.

It was remarked in the last report that "the increased teaching of scientific specific subjects in the higher standards is the natural consequence of the greater attention paid to natural science in the lower part of the schools." Table B shows the correctness of this inference.

It appears that the mathematical subjects still command the most favour on the part of the teachers, Algebra having taken a very remarkable lead. All the physical sciences have increased even more than might have been expected from the increase of scholars. The Principles of Agriculture is the only subject that shows an actual decrease.

Estimating the number of scholars in Standards V., VI., and VII. at 615,000, the percentage of the number examined in these specific subjects, as compared with the number of children qualified to take them, is 26·6; but it should be remembered that many of the children take more than one subject for examination. The following table gives the percentage for each year since 1882, and shows that Science is gradually recovering from the great depression of about eight years ago:—

1882-83 ..	29·0 per cent	1890-91 ..	20·2 per cent
1883-84 ..	26·0 ,,	1891-92 ..	19·7 ,,
1884-85 ..	22 6 ,,	1892-93 ..	20·2 ,,
1885-86 ..	19·9 ,,	1893 94 ..	20·9 ,,
1886-87 ..	18·1 ,,	1894-95 ..	22·7 ,,
1887-88 ..	16·9 ,,	1895-96 ..	24·2 ,,
1888-89 ..	17·0 ,,	1896-97 ..	26 6 ,,
1889 90 ..	18·4 ,,		

The Returns of the Education Department here given refer to the whole of England and Wales, and are for the school years ending with August 31. The statistics of the London School Board are brought up to the year ending with Lady Day, 1898. They also illustrate the great advance that has been made in the teaching of Elementary Science as a class subject, and they give the number of children as well as the number of departments.

Years.	Departments.	Children.
1890-91	11	2,293
1891-92	113	26,674
1892-93	156	40,208
1893-94	183	49,367
1894-95	208	52,982
1895-96	246	62,494
1896-97	364	86,638
1897-98	322	70,626

The last year shows an apparent falling-off in the teaching of this subject, but, as has been mentioned above, the Government having made the giving of object lessons obligatory in the lower standards, 442 departments, with 75,993 children, have already adopted them. This has caused a reduction in the teaching of "Elementary Science" under that name; but, taking the two subjects together, this must be regarded as a very considerable gain.

The Education Department continues to meet the objection against the limitation under the Code by which only two class subjects are allowed to be taught, by adding combined courses of study. This year a new course of this character has been introduced into Schedule II., described as "Elementary Science and Geography Combined." And as, under the present regulations, one of the class subjects must be such as can be taught by means of object lessons in the lower standards, some such subject as the combined one above mentioned must be taken. A copy of the scheme is given in the Appendix, by which it will be seen that in the lower standards the phenomena of the land and water are to be illustrated experimentally as an introduction to Geographical Science.

A similar principle has been adopted in respect of the specific subjects. Hitherto Chemistry has formed a course of itself, and Physics has been divided into two separate courses, the one dealing with Sound, Light, and Heat, and the other with Magnetism and Electricity; but they formed only three out of the nineteen subjects from which choice could be made. A separate course of Elementary Physics and Chemistry combined has now been introduced, which is set out in the Appendix, and which is admirably adapted for experimental investigation at the hands of the students themselves.

The work under the Evening Continuation Schools Code continues to progress, as will be seen from Table C.

It is again evident that the mathematical subjects are rapidly increasing in favour, and that Agriculture is decreasing. It will be noticed with satisfaction that the Science of Common Things is receiving greatly increased attention, but it is a matter of regret that there is a decrease in the time given to Elementary Physiography, and still more so in the case of Elementary Physics and Chemistry. Agriculture would become a more valuable and probably a more popular subject of study if a really good practical course were devised.

An important change has been taking place in Scotland. The code of the Scotch Education Department now admits of the possibility of gaining the full class grant although only two subjects are taken. As one of these must be English, and in the higher standards provision must be made for history or geography or both, the teaching of Science as a class subject has been greatly reduced during the last two years. But a new article in the Code for 1895 offers a special grant of a shilling on the average attendance of boys who are satisfactorily taught "elementary science"; and this has far more than made up the deficiency. In fact the aggregate total of children learning elementary science in the Scotch schools has risen from 34,151 in 1894-95 to 85,671 and 133,855 respectively in the two succeeding years.

Your Committee have frequently referred to the anomaly that pupil teachers are not obliged to receive any instruction in Natural Science, although they may have to give instruction in such subjects, either specifically or in the form of object lessons; indeed, if they should be in charge of a class of the three lower standards it would be obligatory upon them to give such object lessons. A Departmental Committee, consisting of the Rev. T. W. Sharpe, Her Majesty's Chief Inspector of Schools, as Chairman, and several Inspectors and Principals of Training Colleges and Pupil-teacher Centres, have reported upon the pupil-teacher system. They recommend that the age for entering as pupil teachers should be raised, and that the interval between the elementary school and their apprenticeship should be passed at a secondary school. This would by no means ensure that the young people would receive any instruction in Science during that period of their career. No alteration is proposed in the optional Science Course prescribed by the Code of the Education Department, except that the Queen's Scholarship examination is to be limited to the elementary stage of Physiography prescribed in the syllabus of the Science and Art Department. With regard to the College Course the recommendation is singularly weak, Science being placed as an optional subject, without any definite course of study prescribed. For the first two years it is laid down that of the optional subjects not more than two must be taken out of a list of four or six respectively, some of which from their very nature are almost sure to be taken in preference.

TABLE A.

Class subjects—Departments.	1890-91.	1891-92.	1892-93.	1893-94.	1894-95.	1895-96.	1896-97.
English	19,825	18,175	17,394	17,032	16,280	15,327	14,286
Geography	12,806	13,485	14,256	15,250	15,702	16,171	16,646
Elementary Science	173	788	1,073	1,215	1,712	2,237	2,617
Object Lessons	—	—	—	—	—	1,079	8,321

TABLE B.

Specific subjects—Children.	1891-92.	1892-93.	1893-94.	1894-95.	1895-96.	1896-97.
Algebra	28,542	31,487	33,612	38,237	41,846	47,225
Euclid	927	1,279	1,399	1,468	1,584	2,059
Mensuration	2,802	3,762	4,018	5,614	6,859	8,619
Mechanics	18,000	20,023	21,532	23,806	24,956	26,110
Animal Physiology	13,622	14,060	15,271	17,003	18,284	19,989
Botany	1,845	1,968	2,052	2,483	2,996	3,377
Principles of Agriculture	1,085	909	1,231	1,196	1,059	825
Chemistry	1,935	2,387	3,043	3,850	4,822	5,545
Sound, Light, and Heat	1,163	1,168	1,175	914	937	1,040
Magnetism and Electricity	2,338	2,181	3,040	3,198	3,168	3,431
Domestic Economy	26,447	29,210	32,922	36,239	39,794	45,869
Total	98,706	108,434	119,295	134,008	146,305	164,089

TABLE C.

Science subjects.	Units for payment. England and Wales. 1893-4.	1894-5.	1895-6.	1896-7.	London School Board. 1893-4.	1894-5.	1895-6.	1896-7.
Euclid	595	1,086	1,648	2,270	10	29	7	—
Algebra	3,940	6,657	10,374	14,260	316	302	535	714
Mensuration	14,521	32,931	41,772	50,748	279	374	452	369
Elementary Physiography	2,554	4,045	6,590	6 325	37	9	5	—
Elementary Physics and Chemistry	6,500	7,850	6 749	5,183	79	200	152	129
Science of Common Things	6,223	10,350	12,906	18,293	231	262	468	556
Chemistry	3,484	7,814	8,222	9,641	212	455	404	488
Mechanics	841	1,148	1,458	2,196	230	197	209	127
Sound, Light, and Heat	500	1,046	861	1,156	—	15	11	7
Magnetism and Electricity	2,359	4,451	5,073	6,990	662	776	783	939
Human Physiology	5,695	8,395	7,825	10,047	91	68	56	49
Botany	336	547	905	1,080	5	91	97	32
Agriculture	3,579	4,991	4,694	4,061	—	—	—	—
Horticulture	438	1,140	1,812	1,911	—	—	—	—
Navigation	42	69	142	99	—	—	—	—
Totals	51,607	92,520	111,031	134,260	2,152	2,778	3,179	3 410

An important letter has been addressed to the Right Hon. Sir John Gorst by Sir Philip Magnus, the Chairman of the Joint Scholarship Board, in conjunction with the Chairman of its four educational committees. They point out the necessity of securing the proper training of those who will be teachers of scientific subjects, and that the instruction of pupil teachers in Science is now often carried on, under great pressure, by a system of cram, and even by persons who have not themselves any satisfactory knowledge of modern scientific methods. They suggest as a remedy that the first part only of the elementary stage, Physiography, be compulsory; that the teaching of this subject be recognised only where it is given with proper accessories, all pupils performing the experiments in a series of at least twenty-four lessons of two hours' duration; and that inspectors should be required particularly to report whether proper apparatus and accessories are provided.

In last year's report the Committee referred to what Mr. Heller was doing in respect of the teaching of Science in the schools of the London School Board. He has since obtained a better appointment at Birmingham, but the syllabus of lessons which he prepared is still employed in the schools. This of course requires that the masters and mistresses should be qualified for carrying it out, and for this purpose classes of twenty-four hours are conducted for their benefit by the Science Demonstrators. These gentlemen have lately agreed upon two separate syllabuses for masters and mistresses, which follow in general the scheme they are expected to teach to their scholars. The classes of a similar kind that have been carried on hitherto have been appreciated by the teachers, and the Board are increasing their laboratory and other accommodation for the purpose. It is recognised that it will be necessary to continue these teachers' courses for some years, in order to overcome the difficulty which now exists in consequence of the general want of practical experiment in such instruction in Science as has been given in the course of training of most class teachers.

APPENDIX.

Schedule II. — *Course D. Elementary Science and Geography Combined.*

Standards I., II., *and* III.—Annual courses of about thirty object lessons, of which elementary geography should form a part, beginning with the simplest phenomena which the children can observe:—Land, water, the form of the earth, the sea, hills, valleys, rivers, proceeding to notions of locality and distance, and the means of representing all of these by modelling in sand or other

material, and by a map, with special reference to the map of England.

The other object lessons should include some of the various subjects suggested in this Schedule under the head of Elementary Science.

Standard IV. — Geography of England, physical and political.

Lessons on animals and on materials used in agriculture, or in some simple manufactures.

Standard V.—Geography of the British Isles, with some knowledge of India and one or more of the Colonies.

Lessons on means of locomotion, and on processes used in agriculture or manufacture.

Standard VI.—Geography of Europe, physical, political, and commercial.

Lessons on the physical laws that determine climate, animal life, locality of certain industries, &c.

Standard VII.—The work of the preceding years, with special knowledge of the British Empire, and of those portions of the world with which we are engaged in commerce.

Distribution of the races of mankind.

Schedule IV.—*Specific Subjects.* (13.) *Elementary Physics and Chemistry.*

1st stage.—Properties of common stuffs; relative density of solids and liquids; flotation of solids. The barometer and thermometer; their use; graphic representation of daily readings. Solution: water as a solvent; solubility of metals, &c., in acids; crystallisation of salt, soda, alum.

2nd stage.—Evaporation and distillation; heat absorbed in fusion of ice and in conversion of water into steam; density of ice; change in density of water on heating; moisture in air; wet and dry bulb thermometer. Study of iron rusting, and of combustion of candle, gas, oil, phosphorus; effect on metals of heating in air; discovery of active constituent of air.

3rd stage.—Chalk and lime; the burning of chalk or limestone; action of muriatic acid on chalk or limestone; carbonic acid; re-formation of chalk. Discovery of carbonic acid in air; its formation by combustion of carbonaceous materials and in respiration. Study of action of muriatic and vitriolic acids on zinc; combustion of the gas obtained, and discovery of the composition of water. Presence of air and solids dissolved in water; sea water; hardness of water.

THE CYANOMETRIC ESTIMATION OF SOME METALS.

By HARRY BREARLEY and HORACE JERVIS.

(Concluded from p. 179).

Manganese.—This element is precipitated when an insufficient amount of ammonium chloride is present, and, as the precipitation takes place very slowly, it is impossible to take full advantage of the delicacy of the indicator even by repeated filtrations. Such approximations as we were able to make under these circumstances showed that the precipitated manganese oxides did not interfere in any other way. If ammonium chloride be added to keep the manganese in solution there is no interference at all. The manganese may also be precipitated from the solution by using ammonium carbonate instead of ammonia. The manganous carbonate becomes bath coloured and less bulky in form after adding the cyanide, and may then be very readily filtered off. Where the filtration is easy and the precipitate not bulky an aliquot portion need not be filtered off; the nearly finished solution may be repassed through the filter, as is mentioned under zinc.

The harmlessness of manganese should be emphasised, because it has been repeatedly said to render this process of estimating nickel valueless.

Chromium.—The interference of this element cannot be avoided by the use of tartaric acid. The direct titration, in which cyanide is added until the AgI vanishes, cannot be reliably performed, because the indicator disappears long before it should, and the turbidities re-formed with silver nitrate so as to complete the reaction become more and more dense on standing. The reaction between the nickel and the potassium cyanide seems to be retarded by the joint presence of the tartrate and the chrome oxide salts, so it happens that if an excess of cyanide be added the results are the more approximately accurate, as a longer time is allowed to elapse before going back with the silver nitrate; and it may properly be imagined that by adding enough cyanide to quickly complete the reaction, as in the case of the copper titration, and then allowing to stand a while, very approximately accurate results might be obtained. Such a procedure, however, would require some knowledge of the amount of nickel present, and with such information to hand the acid titration may be quite as expeditiously and more accurately employed.

The mixed solution of chromium and nickel salts indicates itself by a change in colour from greenish-blue to full green when the solution is neutralised; the blue tint is recovered by a drop of HCl, and the titration proceeded with. It sometimes happens, particularly when the cyanide contains considerable amounts of carbonates, that a precipitate begins to form before all the cyanide is added. We have not found small precipitates thus formed to interfere. Test analyses for acid titration:—

0·05	0·10 gr. Cr present.
0·1000	0·0999 gr. nickel recovered.

Table I. shows that the interference may also be avoided by converting chromic oxide salts into chromic acid salts. In this case it is only necessary to remark that a reaction between the alkaline chromate and the ammoniacal solution of nickel may precipitate a basic chromate of nickel. This may be obviated by adding ammonium sulphate to the mixture before making alkaline.

Tin.—In the presence of stannous salts a red colouration is produced on adding the cyanide—probably due to the subcyanide of nickel investigated by Moore (CHEMICAL NEWS, lxviii., 295; lxxi., 81). This complication should be avoided by oxidising the stannous to stannic salts, in the presence of which perfectly accurate estimations may be made.

Molybdenum (*Soda Molybdate*).—The results may be falsified by the fact that in an ammoniacal solution the nickel is precipitated by the molybdate in a form which is not readily acted upon by the potassium cyanide. This nickel-molybdenum precipitate forms only very slowly, and is still further retarded by the presence of ammonium sulphate. If the titration is not unduly delayed after making the solution alkaline, the results are perfectly accurate.

Arsenic (*Soda Arsenite*).—The larger amounts of this compound cause the results to be somewhat low. The error is always less than 1 per cent, but it is so persistently a negative quantity that it cannot be well accounted for by experimental error. After converting into arsenate by making slightly acid with nitric acid, adding a little bromine water, boiling off excess, and titrating as usual, we find the results to be perfectly accurate. As with molybdenum, there should be no unnecessary delay between making alkaline and adding the cyanide.

Antimony and Bismuth.—The oxychlorides formed on diluting do not interfere. Their precipitation can be prevented by previously adding a small amount of tartaric acid, after which the direct titration may be accurately employed.

Lead (*Acetate*).—Even when sulphates or chlorides happen to be precipitated, lead does not interfere with the accuracy of the nickel estimation. The precipitates may be obviated by using nitrates instead of sulphates to heighten the iodide turbidity.

Uranium (*Uranyl Nitrate*).—Ammonia throws down a yellow precipitate which soon clogs the filter. It is best to use the carbonate of ammonium, an excess of which re-dissolves the yellow precipitate.

Tungsten (*Soda Tungstate*).—No interference, or other visible indication that any foreign metal is present.

Citric Acid.—This reagent is not nearly so satisfactory as tartaric acid for preventing the formation of precipitates in alkaline solutions. It causes the results to be low.

The Acid Titration.

It is, theoretically, valid to object that potassium cyanide and the double cyanide of nickel and of copper are decomposed in an acid solution. There seems to be no difficulty in always providing a neutral solution from which one may attain any degree of acidity desirable. We prefer to work with a very *slightly* acid solution; but to meet the above objection, and because it is desirable to know the limit of accuracy, the stability of a procedure as it were, we have made some experiments on this point.

To a solution measuring 200 c.c., and containing rather more cyanide than is needed to combine with 0·1 grm. nickel, there was added 10 c.c. HCl (two normal strength), and the whole allowed to stand three or four minutes. On estimating the cyanide the results were always within 0·3 per cent of the truth. In the same way the double cyanides $Ni(CN)_2{\cdot}2KCN$ and $Cu(CN)_2{\cdot}2KCN$ were formed in an alkaline solution. This solution was then made acid, and, like the previous test, allowed to stand. The error with the nickel compound was within 0·2 per cent, and with the copper compound (HCN could be faintly smelled) the worst result was only 0·6 per cent out. It is worthy of remark that while the nickel solution remained clear throughout, a white precipitate was thrown down from the copper solution, which on standing clotted somewhat, and was not then *immediately* re-dissolved on making alkaline again.

This (acid) form of titrating a solution was incidentally applied to eliminate the influence of manganese on the cyanometric estimation of copper (Chem. News, lxxvi., 303). It was there related as a chance observation which had happily overcome a difficulty; its use in the foregoing cases, however, shows it to be so widely applicable as to deserve some consideration.

Already the procedure has eliminated the error from the cyanometric estimation of nickel in presence of chromium, iron, zinc, and aluminium, and from the estimation of copper in presence of manganese. An obvious enquiry is whether the interference of chromium, iron, &c., with the estimation of copper can be avoided in the same way. At present this question must be answered negatively. The enormous error which chromium introduces can in this way be reduced about twenty times, but it has not been altogether eliminated. We are still considering this point.

Taken altogether, the amended results suggest that the interference of chromium, aluminium, and iron, when the estimation of Ni or Cu is performed in the usual way, are due in each case to the carrying down of part of the nickel or copper by the more or less compact precipitates which are formed in an alkaline solution by the interfering elements. It is easy to understand, however the nickel or copper may be associated with the precipitate, that the cyanide can react less readily with the precipitated portions than with the portions remaining in solution—hence the invariable negative value of the interference.*

The proof of this view would require us to show that on making alkaline, part of the copper or nickel is precipitated along with the interfering element, if such were not already well known to be the case. However, the point was submitted to experiment, and, as the results were obtained under comparative conditions, they are interesting.

Each test contained 0·1 grm. Ni, 0·1 grm. of the interfering metals, and an excess of 10 c.c. 2N. ammonia in a volume of 250 c.c. The nickel was estimated in a filtered fraction.

Interfering Metal.	Ni in solution.
Chromium	0·0041
Aluminium	0·0182
Iron	0·0358.

These separations were made under just such conditions as obtained when the corresponding interferences of Table I. were being determined, and it is noteworthy that chromium which carries down most of the nickel interferes most with the cyanometric estimation of nickel, and that aluminium and iron in each case are in the same order,*

We may then reasonably conclude that the acid titration gives improved results, because the double cyanides $Ni(CN)_2{\cdot}2KCN$ and $Cu(CN)_2{\cdot}2KCN$ are formed before the interfering metal is precipitated, and hence the reaction illustrated by the above table is avoided.

If the interference of a precipitable element were obviated by these means, one might not safely conclude that the carrying down caused the error, but they might suspect such to be the case. Such a case is presented by the behaviour of manganese in the cyanometric estimation of copper. From the frequent association of copper and manganese and the extensive use made of the estimation of copper by KCN, this interference has been the subject of much speculation. The issue is somewhat complicated by the fact that the precipitate $(Mn(HO)_2)$ also exerts a reducing action. This latter consideration led Field to explain the results by the formation of a colourless compound of the two metals, and it has been remarked later Chemical News, lxxvi., 303) that Field's suggestion is theoretically valid. The lack of opportunity compels us to reserve this point for further investigation.

Totley, near Sheffield, September 3, 1898.

* Zinc must be taken as an exception, as it can itself react with the cyanide.

ON THE

TRANSFORMATION OF CHEMICAL ENERGY INTO ELECTRIC ENERGY.†

By Prof. F. FOERSTER.

(Continued from p. 182).

The solution of this problem from the commercial point of view encounters two great difficulties. On the one hand, the gas cannot react except when it is in contact with the electrodes and the electrolyte. On the other hand, it is necessary to use very large quantities of gas in very little time, to obtain any considerable amount of electric current. These two questions were recognised by the first chemists who engaged themselves with the problem, when they were endeavouring more to apply the Grove cell commercially than to make carbon cells. Westphal in 1882 saw these difficulties, and in his patent (German patent, No. 22,393) described a number of methods which allowed more particularly an intimate and continuous contact of the gas with the electrodes and the electrolyte. For example, he made the gas pass through porous carbon electrodes, and he also introduced it under the electrolyte by means of slightly inclined tubes open at the lower end, &c. It suffices to mention these pro-

* H. von Jüptner (*Stahl und Eisen*, xiv., 872; *Journ. Iron and Steel Inst.*, 1894, i., 616; ii., 425) calls attention to the fact that Fresenius recommends ammonia for separating small quantities of iron from nickel. Von Jüptner further finds that the process is applicable when the iron is 200 times the weight of the nickel present, and hence may be used in the analysis of steels. Where the steel also contains several percents of chromium, as is occasionally the case, one needs to be reassured of the sufficiency of Jüptner's proposal.

† *Moniteur Scientifique*, Series 4, vol. xii., July, 1898.

posals, as they have not been commercially successful. They do, however, give useful hints to the future worker on the subject. In the same way, the lack of practicable application compels us to pass by Scharf's cell, in which dilute sulphuric acid is used, with carbon electrodes, and in which the electric current is looked for by the combustion, in the cold, of hydrogen, or of hydro-carbides.

We shall, however, examine the Mond and Langer element much more closely (*Zeit. f. Elect.*, iv., p. 139). The first problem presented to these chemists was to accelerate the reaction of the gases, and to achieve this end they made use of a method well known in laboratories —viz., platinum black. We well know that the accelerating action of this substance is based on the faciliity it possesses of condensing the gases on its surface. But, on the other hand, MM. Mond and Langer found that the action of platinum black is weakened by contact with liquids, which forced them to follow, in the construction of their batteries, the principles of the dry battery where the electrolyte is imbedded in porous materials.

For porous materials we can make use of plaster, asbestos, cardboard, &c., which are soaked in the electrolyte and then enveloped in perforated sheets of platinum, or of gold covered with a layer of platinum black. Care must be taken to make the surface of contact between the gas and the platinum black as great as possible. These plates are then connected in such a manner that their surfaces covered with platinum form the greater poles of the cells of which the other pole is composed of two insulated plates. To start the battery we have only to let air enter one-half of the cells, alternatively with hydrogen or hydrocarbides in the other half.

By using hydrogen. Mond and Langer succeeded in transforming 50 per cent of the heat of combustion into electric energy. The cell with an active surface of 700 square centimetres (0·35 grm. of platinum and 1 grm. of platinum black) gave them a current of 2 to 2·5 ampères and 0·73 volt. The principal fault of this apparatus is the uncertainty of its return; the absorption of the gas by the platinum black is very variable and cannot be controlled, and, further, the re-partition of the electrolyte in the porous substance is also subject to variations; and, finally, the construction of the apparatus is rather expensive.

If, in the Mond and Langer cell, the hydrogen is replaced by hydrocarbides, its electromotive force becomes at first much greater; but it falls after a few days, and then remains very low. As was pointed out by Quincke (*Zeit. f. Electr.*, iv., p. 52) this phenomenon may be attributed to the transformation of the hydrocarbides into complicated carbonised acids.

The idea of accelerating the action of the gas by using catalytic materials is of enormous importance in the construction of gas cells, above all when the hydrocarbides, the carbonic oxide, &c., such as they are obtained commercially, as well as the oxygen of the air, are diluted with large quantities of nitrogen. Zettel (*Zeit. f. Elect.*, ii., p. 543), has recently, in the Ostwald laboratory, made some experiments in this direction, for the purpose of finding catalytic materials which would accelerate oxidation. His work, however, has not been successful, but he was able to note one interesting phenomenon: his cell—which consisted of a sheet of platinum covered with platinum black, plunged partly into weak sulphuric acid, and connected with a copper plate—showed a very sudden decrease of electromotive force, as soon as the current exceeded a certain limit. This phenomenon may be explained by taking note of the fact that the absorbing power of the platinum black for the gas is limited, and that in this case the oxygen only acts in the condensed state; the effective action of the cell should therefore diminish when the oxygen is consumed more quickly than it can be absorbed by the platinum.

Further, this experiment shows that platinised platinum, besides its high price, has the disadvantage of only acting very slowly.

In the year 1894, Borchers, working on an idea of Ostwald's, proposed an altogether model method for the construction of a carbon element. He first endeavoured to find an electrolyte which could keep carbonic oxide and the hydrocarbides in solution. Under this heading chloride of the protoxide of copper, in either commercial or acid solution, presents, as we know in gas analysis, great advantages.

A glass cell, divided into three compartments by perforated partitions, so as to allow free communication throughout, was filled with a solution of cupreous chloride. In the two outside compartments, carbonic oxide or coal-gas was introduced by means of copper tubes; the middle compartment contained a carbon cell, by which air was introduced. Borchers was enabled to get an electromotive force of 0·4 volt through a resistance of 50 ohms.

However, it was soon noticed that this cell produced electrical energy without forming carbonic acid, from which it was concluded that here the electric energy was produced, not by the combustion of the gas, but by other reactions, among which the most important would be the solution of the copper tube in the chloride.

(To be continued).

THE

ACTION OF LIGHT UPON DYED COLOURS.*

(Continued from p. 177).

Class III.—Moderately Fast Colours. (Wool).

The colours of this class show distinct fading at the end of the second period (August 22 to September 29, 1896), which becomes more pronounced at the end of the third period (September 29 to November 5, 1896). A pale tint remains at the end of the fourth "period of exposure" November 5, 1896, to May 22, 1897), and at the end of a year's exposure the colour has entirely faded, or at most only traces of colour remain.

Azo Colours.

Wool Book XII.

Acid Colours.—

*3. Azo Acid Brown. Constitution not published.
6. Fast Brown. From xylidine-mono-sulphonic acid and α-naphthol. S. and J. II. 80.
12. Fast Brown. From naphthionic acid and resorcinol. S. and J. III. 164.
14. Diamond Brown. Constitution not published.

Direct Cotton Colours.—

7. Congo Brown G. From sulphanilic acid and benzidine, with resorcinol and salicylic acid. S. and J. III. 269.
9. Thiazine Brown G. Constitution not published.
12. Congo Brown R. From α-naphthylamine-sulphonic acid L and benzidine, with resorcinol and salicylic acid. S. and J. III. 270.
14. Hessian Brown 2BN. Constitution not published.
16. Hessian Brown 2B. From sulphanilic acid and benzidine with resorcinol. S. and J. III. 277.
17. Thiazine Brown R. Constitution not published.
20. Diamine Bronze G. From benzidine, with salicylic acid and amido-naphthol-disulphonic-acid-H-azo-*m*-phenylene-diamine. S. and J. III. 263.
41. Diamine Brown M. From benzidine with salicylic acid and γ-amido-naphthol-sulphonic acid.
43. Diamine Brown B From benzidine, with phenyl-γ-amido-naphthol-sulphonic acid.
45. Benzo Dark Brown. Constitution not published.

* Report of Committee, consisting of Dr. T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Bristol Meeting, 1898.

Direct Cotton Colours Developed.—

*1. Diamine Cutch. Constitution not published. Naphthylene Violet azotised and developed with sodium carbonate. S. and J. III. 256.

Azoxy Colours.

Direct Cotton Colours.—

22. Mikado Brown 2B. Constitution not published.
23. Mikado Brown G. Constitution not published.
24. Mikado Brown B. Constitution not published.

Natural Colouring Matters.

Wool Book XIII.

Mordant Colours.—

*Ventilago (Cu) (Fe). Ventilago madraspatana (root-bark).
Sanderswood (Cu) (Fe). Pterocarpus santalinus (wood).
Barwood (Cu) (Fe). Baphia nitida (wood).
Camwood (Cu) (Fe).

Notes.—Diamine Brown M loses its reddish hue and becomes apparently darker during the first "fading period"; the altered colour fades slowly, and finally leaves at the end of the year a pale drab colour. Azo Acid Brown acquires a more yellowish hue during the first "fading period"; the colour then fades very gradually without further change of hue, leaving at the end of a year a very pale brown. It might fairly well be classed as a "fast colour." The Mikado Browns are by no means so fast to light as the Mikado Oranges and Yellows; they experience the greatest change in depth of colour during the first "fading period"; the altered colour, which is yellower than the original one, then fades very gradually, and leaves at the end of the year a fairly good buff colour.

Class IV.—Fast Colours. (Wool).

The colours of this class show comparatively little fading during the first, second, and third periods. At the end of the fourth "period of exposure" a pale shade remains, which at the end of the year's exposure still leaves a pale shade.

Azo Colours.

Wool Book XII.

Direct Cotton Colours.—

5. Toluylene Brown G. From toluylene-diamine-sulphonic acid and *m*-phenylene-diamine. S. and J. III. 241.
6. Direct Cotton Brown R. From amido-nitroso-stilbene-disulphonic acid and aniline.

Natural Colouring Matters.

Wool Book XIII.

Mordant Colours.—

12. Cochineal (Cr). Coccus cacti (insect).

Class V.—Very Fast Colours. (Wool).

The colours of this class show a very gradual fading during the different periods, and even after a year's exposure a moderately good colour remains.

Oxyketone Colours.

Wool Book XIII.

Mordant Colours.—

Alizarin Bordeaux B (Cr) (Cu). Tetra-oxy-anthraquinone (1 . 2 . 5 . 8). Quinalizarin. S. and J. III. 403.
Alizarin Bordeaux G (Cr) (Cu).
Alizarin Bordeaux GG (Cr) (Cu).
Alizarin Maroon (Cr) (Cu). Amido purpurin. S. and J. III. 394.
Alizarin Brown (Cr) (Fe). Diamido-alizarin.
Anthracene Brown (Cr) (Fe). Tri-oxy-anthraquinone (1 . 2 . 3) Anthragallol. S. and J. III. 396.

Natural Colouring Matters.

Wool Book XIII.

Mordant Colours.—

Morinda Root (Cr) (Cu) (Fe). Morinda citrifolia (root).
Mang-kudu (Cr) (Cu) (Fe). Morinda umbellata (root-bark).
Chay Root (Cr) (Cu) (Fe). Oldenlandia umbellata (root).
Munjeet (Cr) (Cu) (Fe). Rubia cordifolia (root).
Madder (Cr) (Cu) (Fe). Rubia tinctorum (root).
Lac-dye (Cr) (Cu) (Fe). Coccus ilicis (insect).
Cochineal (Cu) (Fe). Coccus cacti (insect).

Additional Colours.

Oxidation Colour.—

Chromogen I. (1 . 8) Dioxy-naphthalene-(3 . 6)-disulphonic acid; oxidised with bichromate of potash. S. and J. III. 504.

(To be continued).

A TABLE OF ATOMIC WEIGHTS.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 183).

An important deviation from the usually accepted figures is to be seen in the value assigned to platinum below. Our knowledge of the atomic weight of this element depends chiefly upon the elaborate and carefully executed work of Seubert (*Ber. d. Chem. Ges.*, 1881, xiv., 865) and Halberstadt (*Ibid.*, 1884, xvii., 2962), and the only question is how this is to be interpreted. These chemists studied the platinchlorides and platinbromides of potassium and the platinchloride of ammonium, weighing these compounds and some of the products of their decomposition. The careful study of the results shows at once that some source of error lies hidden in all the data, for the various ratios are not wholly consistent, even in any one series. Any value from 194·7 to 196·0 may be obtained from the figures (Clarke, "Re-calculation," 1897, p. 334), the results of Seubert's work being the least discordant among themselves. Dittmar and McArthur (*Trans. Roy. Soc. Edinburgh*, 1887, xxxiii., Part II., 561) explain the discrepancy in the case of potassic platinchloride by assuming that the complex salt contains traces of hydroxyl replacing the halogen and traces of hydrogen replacing the potassium, as well as a small amount of extra occluded potassic chloride. They adduce experimental evidence in proof of this view, but Seubert showed in his reply (*Ber. d. Chem. Ges.*, xxi., 2179) that their hypotheses can hardly be applied to his determinations. Most of Seubert's and Halberstadt's inconsistencies may be explained by the supposition that the complex salts, like all substances crystallised from aqueous solution, contain certain traces of mother-liquor held in minute cells within the crystal structure, and that these traces of water are not free until the substance is disintegrated. I have accumulated a large amount of experimental evidence, soon to be published, upon this subject. Water is one of the most dangerous, although one of the least heeded, impurities in this kind of work; and in my opinion it is responsible for the lack of agreement in this case. Hence the best data for the calculation of the atomic weight of platinum seem to be those concerning the relation of the metallic platinum to the potassic chloride or potassic bromide formed by the decomposition of the complex salts, for the water must surely have been expelled from these products of the ignition. According to Clarke ("Re-calculation," page 333) potassic platin-

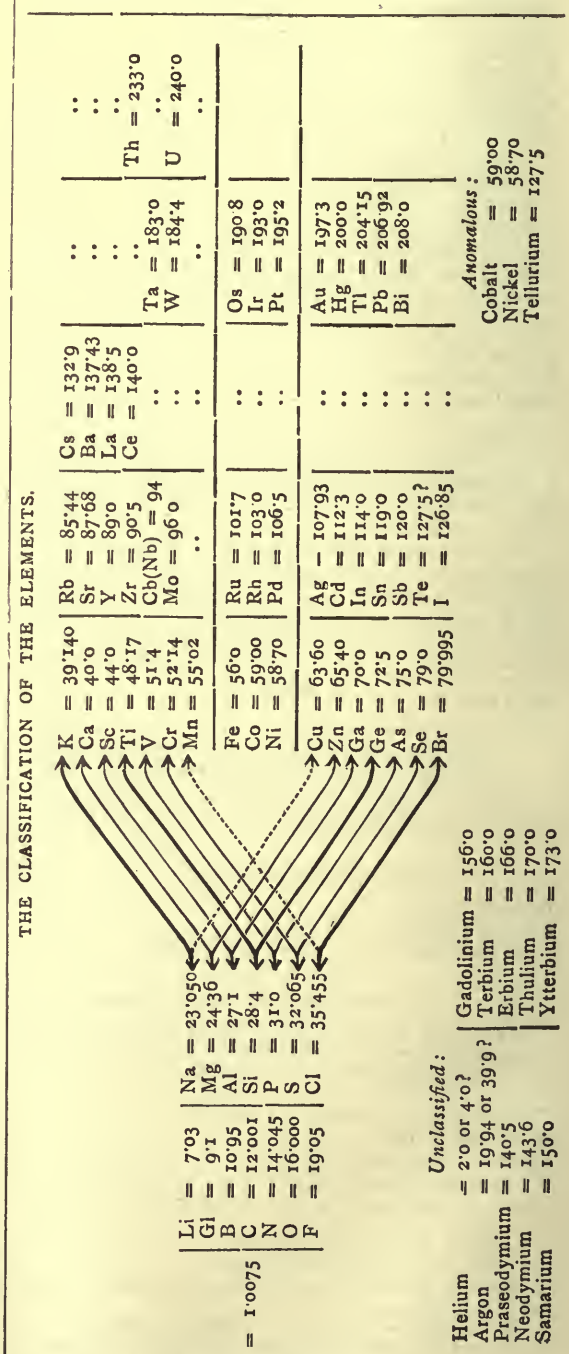
* Presented to the American Academy of Arts and Sciences, March 9, 1898. From the *American Chemical Journal*, xx., No. 7.

A TABLE OF ATOMIC WEIGHTS

OF SEVENTY-FOUR ELEMENTS.

Compiled in March, 1898, from the Most Recent Data.

Name.	Symbol.	Atomic weight.
Aluminium	Al	27·1
Antimony	Sb	120·0
Argon	A	39·9 ?
Arsenic	As	75·0
Barium	Ba	137·43
Beryllium	Be=Gl	9·1
Bismuth	Bi	208·0
Boron	B	10·95
Bromine	Br	79·955
Cadmium	Cd	112·3
Cæsium	Cs	132·9
Calcium	Ca	40·0
Carbon	C	12·001
Cerium	Ce	140·0
Chlorine	Cl	35·455
Chromium	Cr	52·14
Cobalt	Co	59·00
Columbium	Cb=Nb	94·0
Copper	Cu	63·60
"Didymium"	Nd+Pr	142 ±
Erbium	Er	166·0
Fluorine	F	19·05
Gadolinium	Gd	156·0 ?
Gallium	Ga	70·0
Germanium	Ge	72·5
Glucinum	Gl=Be	9·1
Gold	Au	197·3
Helium	He	4·0 ?
Hydrogen	H	1·0075
Indium	In	114·0
Iodine	I	126 85
Iridium	Ir	193·0
Iron	Fe	56·0
Lanthanum	La	138·5
Lead	Pb	206·92
Lithium	Li	7·03
Magnesium	Mg	24·36
Manganese	Mn	55·02
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	143·6
Nickel	Ni	58·70
Niobium	Nb=Cb	94·0
Nitrogen	N	14·045
Osmium	Os	190 8
Oxygen (standard)	O	16·000
Palladium	Pd	106·5
Phosphorus	P	31·0
Platinum	Pt	195·2
Potassium	K	39·140
Praseodymium	Pr	140·5
Rhodium	Rh	103·0
Rubidium	Rb	85·44
Ruthenium	Ru	101·7
Samarium	Sm	150·0
Scandium	Sc	44·0
Selenium	Se	79·0
Silicon	Si	28·4
Silver	Ag	107·93
Sodium	Na	23·050
Strontium	Sr	87·68
Sulphur	S	32·065
Tantalum	Ta	183·0
Tellurium	Te	127·5
Terbium	Tb	160·0
Thallium	Tl	204·15
Thorium	Th	233·0
Thulium	Tu	170·0 ?
Tin	Sn	119·0
Titanium	Ti	48·17
Tungsten	W	184·4
Uranium	U	240·0
Vanadium	V	51·4
Ytterbium	Yb	173·0
Yttrium	Yt	89·0
Zinc	Zn	65·40
Zirconium	Zr	90·5



chloride yields 40·101 per cent of platinum and 30·671 per cent of potassic chloride,—the means of the closely agreeing results of Seubert and Halderstadt,—while, according to Halberstadt, potassic platinbromide yields 25·915 per cent of platinum, and 31·591 per cent of potassic bromide. Disregarding the weight of the complex salt, and assuming that KCl=74·595, and KBr=119·095, it is easy to calculate the respective values 195·06 and 195·39 for platinum. The mean of these two values, 195·2, is given below, instead of Clarke's 194·89. The possible occlusion of potassic halide by the complex salt may render even 195·2 too low; but more investigation is evidently needed to prove this.

The same errors may enter into the work on other platinum metals; indeed Seubert (*Ann. Chem., Liebig*, cclxi., 262) admits that traces of water were contained in some of his salts, but he applies no correction for this serious cause of inaccuracy. Since, however, Clarke's method of combining the discordant results seems more nearly to eliminate the error in these cases, his values for these elements are but little changed in the table.

Feeling wholly unable to decide the present controversy between the two conflicting values (184·9 and 184·0) now proposed for tungsten, I have chosen the mean 184·4 as a compromise which cannot be much more than 0·3 per cent out of the way (compare Hardin, *J. Am. Chem. Soc.*, xix., 657, 1897.

Uranium, the highest of all the atomic weights, is one of the least satisfactorily determined. Recent investigation upon this subject at Harvard seems to show that all the published data are complicated by constant errors, which, however, sometimes partly eliminate one another: accordingly the round number 240, instead of Clarke's 239·59, is printed in the table. The discussion is better deferred until our work has taken more definite shape.

Besides these seven elements, there are seventeen more whose atomic weights, as given in the following table, differ from the results of Professor Clarke's computations by one part in a thousand or more. As none of the seventeen values is known certainly to within one part in five hundred, and some of them are probably at least as much as 1 per cent in error, differences in these cases will excite no especial remark. The elements are:—Cerium, columbium, erbium, gadolinium, gallium, glucinum, indium, lanthanum, neodymium,* osmium, palladium, praseodymium, samarium, scandium, thorium, ytterbium, and zirconium. This is by no means a complete list of the uncertain elements, but only of those for which the data admit of slightly different interpretations.

It is rather unfortunate that most classified tables of the elements omit the fractional parts of the atomic weights, for these fractions will undoubtedly play an essential part in the ultimate solution of the de-Chancourtois-Newlands-Mendeleeff-Meyer mystery. In order to present a modern table which will supply these omissions, as well as afford at a glance an approximate idea of the probable error in each case, I have repeated the values in the natural order. From the classified table have been omitted several elements whose atomic weights and properties are uncertain; their presence in the system serves rather to obscure well-known relations than to elucidate new ones. That this procedure is an omission of incompleteness is evident; the last part of the table is at best a lame affair. The form proposed by Thomsen (*Ztschr. Anorg. Chem.*, ix., 190) is perhaps the most generally satisfactory of the current modes of arrangements, but his last row is unwieldy both for printing and for thinking. In the accompanying table a compromise has been adopted which cannot fail to be comprehensible; it is not my purpose here to enter into the arguments regarding the adequacy of the various forms.

This table will be reprinted, with any changes which may be necessary, every year. Since the commencement of the work I have been glad to hear of the appointment of a Committee by the German Chemical Society to accomplish a similar purpose, the American Chemical Society having for several years possessed such a Committee. The matter cannot receive too much intelligen- examination.

* Since the publication of this paper in the *Proceedings of the American Academy*, H. C. Jones has published a research upon the "dymia" which far exceeds in accuracy and completeness the vague statements of their first separater. Oddly enough, the new values are the old ones interchanged. While it is impossible to say how nearly the new figures represent the peculiarly elusive values in question, they carry with them much greater weight than the old ones, and are given, as far as the first decimal place, in the accompanying table. (See *Am. Chem. Journ.*, xx., p. 345). The value 142 for the mixture "didymium" is also given for convenience in the calculation of analyses in which it is not possible to separate the twins.

NOTICES OF BOOKS.

Radiation. An Elementary Treatise on Electromagnetic Radiation, and on Röntgen and Cathode Rays. By H. H. Francis Hyndman, B.Sc. (Lond.). With a Preface by Professor Silvanus P. Thompson, D.Sc., F.R.S.

The introductory note by Professor Thompson is sufficient to stamp the book as beyond the usual sphere of recent publications on this subject, and its perusal fully justifies the expectation.

Although professedly elementary, the subject-matter is very sound, and the manner in which it is handled carries with it a refreshing sense of originality that makes the book very easy reading.

Starting with the fundamental principles of Radiation, Part I. is devoted to Material Vibrations, longitudinal and transverse; and in Part II. the ether theory is very clearly and simply elucidated, occupying about 120 pages of valuable and interesting matter. The latter half of the book is devoted to Cathode and Röntgen radiation, and is thoroughly up-to-date, and what strikes one very forcibly is the complete absence of sensationalism which usually characterises publications on this subject; there is not even a radiograph of a hand or the picture of an induction coil by a popular maker!

The references to the original papers make this section very valuable. There is a short chapter on Becquerel's Rays, and finally an account of the experiments of Gustave le Bon on "Dark Light."

While we consider the book to be one of the best that has appeared of its class since Röntgen's discovery, there are, unfortunately, one or two errors, chiefly clerical, that we must point out. An amusing one is on page 46, where the ether is said to be "incomprehensible": this, although possibly correct, is probably a misprint for incompressible. On page 167 we read "Radiant electrode matter, or negative rays of Crookes." The term "Radiant electrode matter" is not due to Crookes, whose contention is that the Radiant matter of a highly exhausted vacuum tube is not necessarily electrode matter, but may be purely gaseous. At page 200 we think the author is rather hasty in the statement that Cathode rays "do not affect the eye, and produce no sensation on the skin"; and on page 208 there is a serious mistake, which looks as if a proof-sheet had got astray, for, commencing to describe the "focus tube" as designed by Mr. Herbert Jackson, the description goes on to another and totally different piece of apparatus, where the Cathode stream is focussed on to the glass wall of the tube. This is unfortunate, and will cause some little confusion to the uninitiated. On page 210 a reference is given to *Nature*, June, 1896, which should have been July—describing a form of X ray tube which is said to be of a "markedly improved form," but we cannot help thinking that those who know the difficulties of producing sufficiently high vacua for Röntgen rays would hesitate to accept the recommendation.

These, however, are small matters, and beyond the error on p. 208, already referred to, in no way detract from the value of the book. While commending it to any who wish for sound elementary instruction on the principles of Radiography, we can heartily indorse the concluding sentence of Professor Thompson's preface—"It is much too good to be of use to one whose highest aim is to pass examinations."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 25, June 20, 1898.

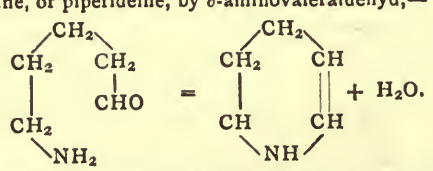
Boiling-point of Liquid Ozone.—L. Troost.—Already inserted in full.

The Preparation of Crystallised Calcium.—Henri Moissan.—Already inserted in full.

A New Gas in the Atmosphere.—W. Ramsay and M. W. Travers.—This has already been noticed in our columns.

Sulphoantimoniates of the Alkaline-earthy Metals.—M. Pouget.—In following up the study of the sulphoantimoniates, the author has acted on the alkaline-earthy sulphides with sulphide of antimony, and has found that a number of compounds are formed with the salts of barium, strontium, and calcium. All these compounds are easily oxidised in contact with air, and should therefore be prepared in a current of hydrogen. The reaction permits of the preparation of ortho- and pyro-sulphantimoniates. Analogies between calcium and strontium are found in the pyro-compounds, and between strontium and barium in the ortho-compounds.

Pyridic Bases.—Marcel Delépine.—Most methods of synthesising the pyridic derivatives consist in the elimination of water between an amine function and an aldehydic or acetonic function, and thus allowing them to become joined to the nitrated functions derived from the aldehyds. The author has here restricted himself to the study of pyridine itself and to that of its hydrides. These first terms give very little direct synthetical action which could be considered as resulting from the unique junction between the aldehydic and the nitrogenised function; but one extremely important one exists, inasmuch as it constitutes at the same time the bond which unites the fatty and the pyridic series; it is the synthesis of tetrahydropyridine, or piperideine, by δ-aminovaleraldehyd,—



It is true that piperidine, C_5H_9N, is only well known under its polymerised form, $(C_5H_9N)_2$; but the author thought it advisable to open the research with a view to finding the thermochemical reactions which exist in this series. For this purpose he took up the study of pyridine, piperidine, chloropiperidine, piperideine, and δ-aminovaleraldehyd, with the results given in this paper.

Some Bases derived from Piperidine.—G. André.—The author has made a fresh study of the bases derived from piperidine and the ethylenic carbides, such as ethylene, propylene, and its isomer, trimethylene. He has also examined the new oxygenised derivatives of glycerin. All these bodies are bi-nitrated; those derived from the carbides do not contain any oxygen, but those derived from glycerin do. The bases examined were:—Dipiperidine-ethylene, $(C_5H_{10}N)_2C_2H_4$; dipiperidine-methylethylene, $C_5H_{10}N.CH(CH_3).CH_2.C_5H_{10}N$; dipiperidine-trimethylene, $C_5H_{10}N.CH_2.CH_2.CH_2.C_5H_{10}N$; and several others.

Bromised Derivatives of Morphine.—H. Causse.—The bromised substitution of morphine as a definite compound seems to be limited to the fourth degree. This result agrees with certain experiments on oxidation which will be published later on. When bromising takes place in concentrated hydrobromic acid, the action of the bromine is regular, and gives rise to crystalline compounds; finally, the tetrabromomorphine behaves as a base or an acid. This last property is not possessed by tribromomorphine.

Some New Aromatic Diurethanes from Piperazine.—MM. Cazeneuve and Moreau.—In a recent paper the authors described their work on the phenylic, gaïacolic, naphtholic α- and β-derivatives, they now complete this series by the description of the derivatives of orthochloric phenol, thymol, and the ortho-, meta-, and para-cresols.

Action of Chlorine on Chloride of Ethylene in the presence of Chlorids of Aluminium. The Chloridation of Acetylene.—A. Mouneyrat.—A long paper, not suitable for abstraction; but the author describes his experiments carried out with a view to determining the constitution of the product resulting from the chlorisation of $(CH_2Cl—CH_2Cl)$ in the presence of this synthetic agent.

Synthesis of Symmetric Tetramethylglutaric Acid.—E. E. Blaise.

Crystallised Compound of Acetylene with Cuprous Chloride.—M. Chavastelon.—When, in the preparation of pure acetylene, we pour hydrochloric acid on moist acetylide of copper, we notice that the latter dissolves without any appreciable disengagement of gas if we take care to cool the mixture during the operation, but under the influence of heat acetylene is produced. It must therefore be admitted that there is a temporary formation of a compound—destroyed by heat—of acetylene and chloride of copper. It can be formed in a hydrochloric solution of cuprous chloride or in an aqueous or alcoholic solution of cupric chloride in the presence of copper.

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THE CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

Edited by Sir WILLIAM CROOKES, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2030.

ETHERION : A NEW GAS.

By CHARLES F. BRUSH.

On the 3rd inst. Mr. Brush read a paper on his newly-discovered gas before the Chemical Society of Cleveland, U.S.

The author commenced by saying that, at the very start, he encountered difficulties in the absence of a means to produce the very low pressures he needed, and to surmount these difficulties he invented the best mechanism for this purpose yet used.

"The purpose of this purely preliminary is to announce the discovery of a new gas, presumably elementary, and possessed of some extraordinary properties. It is a constituent of the atmosphere, and is occluded by many substances. Its chief characteristic thus far ascertained is enormous heat conduct vity at low pressures. In order to appreciate this phenomenon it is necessary to consider the heat conductivity of some of the well known gases.

"A year ago I had the honour to read before this Section a paper on the transmission of heat by gases, and illustrated by numerous curve sheets showing the heat conductivity of several gases at all pressures from atmospheric down to the best vacuum obtainable; also an allied paper on the measurement of small gaseous pressures.

"The apparatus used for the described experiments in heat transmission consisted in part of a long-stemmed thermometer hanging in a long-necked glass bulb, the bulb of the thermometer being in the centre of the glass bulb. Two bulbs were used for different experiments, the

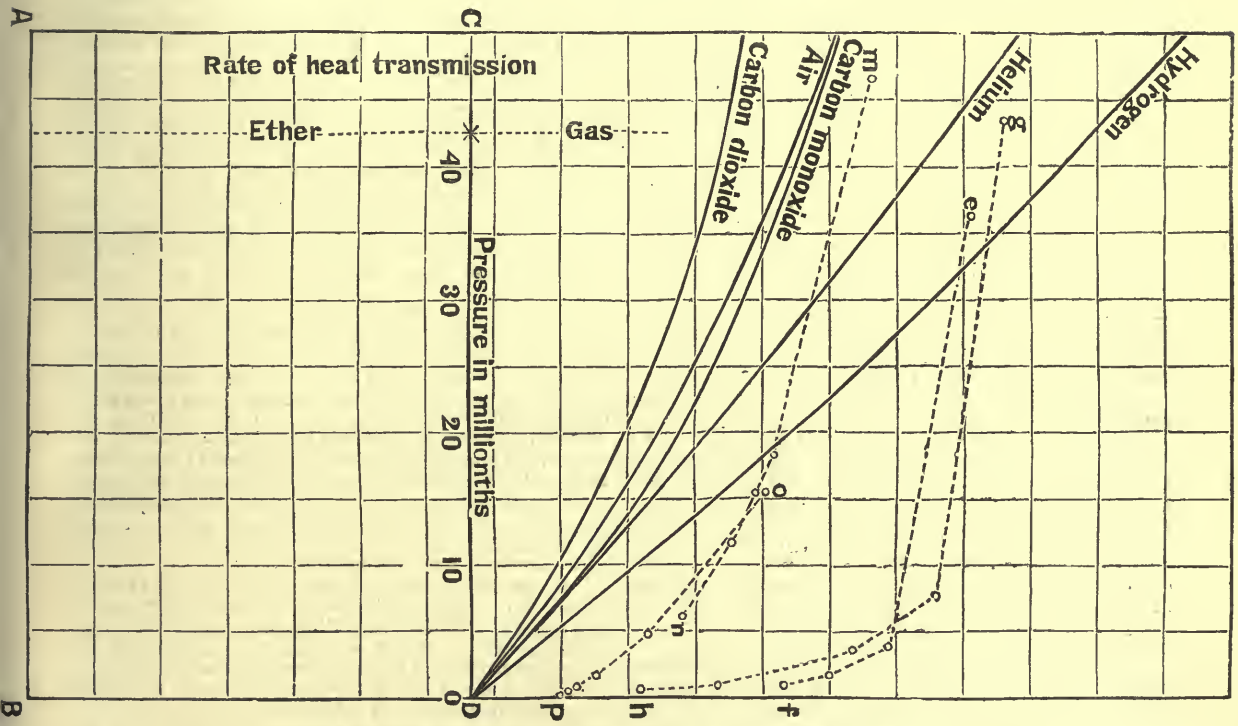


Chart showing Relative Heat Conductivity of Gases.

When he came to examine air at very low pressures and under certain conditions for its heat conductivity, in his chart plotting he was brought to draw several lines, the dotted ones in the chart given herewith, which could be accounted for by no lines of the known gases, like the continuous lines of the diagram. Thus the existence of a new gas was indicated.

Since *Etherion*, as Mr. Brush named the new gas, has no known chemical effect on familiar elements, and will thus not burn or form combinations, it would probably always have remained unknown did it need to depend for discovery on the usual chemical experiments. It was by his entrance into a new field of investigation that Mr. Brush encountered evidence of its existence.

The chart herewith reproduced is that which accompanied his full paper, read first before the American Association for the Advancement of Science, at Boston, on August 23, 1898. An extract from this paper follows:—

larger one 112 m.m. in diameter, the smaller one only 20 m.m. A tank of water and crushed ice under the bulb was adapted to be raised when desired, so as to immerse the bulb in the cold mixture. The neck of the bulb was connected with an air pump capable of reducing the internal pressure to a very small fraction of a millionth of atmospheric pressure; also with an elaborate pressure gauge adapted to measure small pressures with very great precision, and a barometric gauge for measuring larger pressures.

"The present chart shows curves representing the heat conductivity of several gases, from fifty-millionths of atmospheric pressure downward.

"A very brief account of the circumstances which led to the discovery of the new gas may not be out of place. I had long been engaged in high vacua experiments, and had observed that glass apparatus, when highly exhausted and heated, involved gas for an indefinite length of time,

—rapidly at first, then slower, but never stopped until the temperature was reduced. On cooling, rapid re-absorption always took place, but was never complete; indicating that two or more gases had been evolved by heating, one of which was not absorbed on cooling. In other words, the absorption was selective.

"The truth of this conclusion was abundantly demonstrated subsequently. However, the percentage of re-absorbed gas was so large that I used a small quantity of pulverised glass, in several experiments, to absorb a part of the residual gas after the highest attainable exhaustion was reached. The pulverised glass was always lead glass like that of the apparatus, and was heated nearly red-hot for several hours before and during the final exhaustion.

"During these experiments a curious phenomenon was noted; the pulverised glass lost its snowy whiteness. This I thought must be due to reduction of some of its lead; probably by hydrogen evolved on heating. If so, I argued that the hydrogen must have been absorbed from the atmosphere since the manufacture of the glass; and its presence in the glass, if proved, would be a long step toward proving the normal presence of hydrogen in the atmosphere.

"Following the line of experiment thus suggested, I prepared a quantity of pulverised soda glass free from lead, and placed about 120 grms. of it in a large combustion tube connected with the apparatus already described. The combustion tube was adapted to be heated by a gas furnace with automatically regulated gas supply, so as to be maintained at any desired temperature.

"While prepared to make analysis in the usual way of the gas evolved by the pulverised glass in case it appeared in sufficient quantity, I relied chiefly on its heat conductivity for the detection of any large proportion of hydrogen in the last few millionths, not being prepared at that time for spectroscopic examination; and thinking that perhaps some hydrogen might be evolved in the last stages of exhaustion before heating, I tested the conductivity of the residual air from time to time as the preliminary exhaustion progressed.

"When the exhaustion approached a good vacuum, an astounding phenomenon developed. At 36-millionths pressure, the residual gas conducted heat twice as well as air, and nearly as well as hydrogen, at 3·8 millionths it conducted seven times as rapidly as hydrogen, at 1·6 millionths fourteen times, and at 0·96 of one millionth twenty times as rapidly. These results are plotted in the curve *e f*. I did not carry the exhaustion lower than 0·96 m. At this pressure, the time of cooling of the thermometer from 15° to 10° was only 177 seconds, while pure hydrogen would have required 288 seconds.

"Evidently a new gas of enormous heat conducting capacity was present, mixed with the last small portion of air. It must have come from the pulverised glass, and probably formed only a small fraction of the mixture. The last cubic centimetre of gas pumped out was collected, and upon subsequent analysis of it nothing but air was found.

"The discovery of the new gas as above outlined was made nearly a year and a half ago, on March 10th, 1897. On the following day the pressure had increased to nearly five-millionths; while the time of cooling of the thermometer, instead of diminishing as usual with increase of pressure, had risen from 177 seconds to 245 seconds, showing that the new gas had largely disappeared. This was subsequently found to be due to absorption by the phosphorous pentoxide used in desiccation.

"Long-continued moderate heating of the pulverised glass caused the evolution of some air, much carbon dioxide and hydrogen, some carbon monoxide, and more of the new gas. The selective absorption which occurred on cooling was confined almost wholly to the hydrogen and the new gas. After further moderate heating and thorough exhaustion, I raised the temperature, continued the exhaustion, and got the results embodied in the curve *g h*, showing that much of the new gas was present: the conductivity at 0·38 of a millionth, the last station in the curve, being twenty-seven times that of hydrogen! Several days of high heating, with frequent exhaustion, failed to wholly deprive the pulverised glass of its new gas, though the output was greatly diminished. For this and other reasons I believe that the new gas resides in, and not simply on, the surface of glass.

"A rejuvenation of pulverised glass by exposure to the air, in connection with the results obtained by the diffusion of air, leaves no room for doubt that the new gas is a constituent of the atmosphere.

"Several other substances than glass were examined, and nearly all found to contain the new gas.

"When the new gas was present the form of the conductivity curves was very different from those of the known gases, the effect of the new gas becoming more prominent as the pressure was reduced. I do not doubt that this was due to the interference of the heavier and slower moving molecules of the ordinary gases always mixed with the new gas. When the new gas is obtained in a state of purity, I expect to find its curve of heat conductivity similar to those of hydrogen and helium, but with immensely increased ordinates.

"Believing that the new gas is very much lighter than air or hydrogen, and may therefore be separated from the atmosphere by successive diffusions, I have spent several months in experiments with this end in view. Quite recently my efforts have been crowned with most promising success. The difficulty has been to find a suitably porous septum; one free from holes, and sufficiently fine grained to prevent more than a very slow passage of air, while a considerable surface is exposed to the atmosphere on one side, and to a fairly good vacuum on the other.

"The best results have been obtained with porous porcelain having its superficial pores nearly closed by suitable treatment. A tube of this kind, closed at one end, was connected with the apparatus, and the whole kept exhausted to a pressure of 1·3 m.m. About 19 c.c. of gas was diffused per hour. After thirty-six hours, the diffusion tube was shut off, the exhaustion continued, and data for the *m n* curve obtained. It was found impracticable to carry the exhaustion below 6 millionths, because of the presence of moisture, which interfered with the action of the pump—no desiccating agent being used. As both phosphorus pentoxide and soda-lime absorb the new gas, they cannot be used for desiccation.

"If the exhaustion had been carried as far as in the curve *o p*, it is probable that a higher conductivity than in that curve would have been shown, *i.e.*, a conductivity more than forty-two times that of hydrogen, or something like a hundred times that of air. Here we have the heat conductivity of air at very low pressure increased something like a hundredfold by one diffusion.

"I have not yet tried a secondary diffusion, but feel confident that successive diffusions of air will afford a practicable means of obtaining the new gas in a state of approximate purity."

HELIUM IN THE ATMOSPHERE.

The following letter appeared in last week's *Nature*:—

"The letter of Mr. Baly in your issue of last week, corroborating the statement of Friedlander and Kayser that helium is a constituent of the atmosphere, induces me to put on record a further confirmation of the accuracy of this observation. Having had the opportunity, on June 20 last, of examining samples of the more volatile portions from liquid air, which had been handed to me by Prof. Dewar, I had no difficulty in seeing the lines of helium in them. Further, a sample of the helium separated by Prof. Dewar from Bath gas (following the

discovery of Lord Rayleigh) undoubtedly contained the substance called neon.

"In giving these facts I am only confirming the observations of Prof. Dewar given to me in letters accompanying the samples of gas.

WILLIAM CROOKES."

October 11.

FURTHER EXPERIMENTS ON THE ABSORPTION OF THE RÖNTGEN RAYS BY CHEMICAL COMPOUNDS.*

By Dr. J. H. GLADSTONE, F.R.S., and WALTER HIBBERT.

THIS paper has for its object a description of experiments on the absorption of Röntgen rays by metals and metallic salts. It is in continuation of what has been reported at the two previous meetings of the British Association.

During the past year we have had two purposes in view. 1. To perfect the quantitative methods employed for estimating the comparative intensity of radiographs taken simultaneously. 2. To determine whether the amount of absorption is fairly an atomic phenomenon, or whether the amount of rays absorbed by a compound body depends to any extent on its physical condition or manner of combination.

We have again employed the Lummer-Brodhun photometer, and have endeavoured to insure as much regularity in the amount of exposure as possible, by placing the objects that were simultaneously exposed at a considerable distance from the radiating point, usually about 15 inches, and by rotating them during the experiment. We believe that in this way the effect upon the sensitive plates can be determined within ± 2 per cent. In order further to reduce the effect of unavoidable irregularities, each experiment was usually repeated about six times, and the mean was taken. By the kindness of Mr. Wimshurst one of his machines was sometimes employed, as it was found to give a steadier effect than the Ruhmhorff coil.

Among the results arrived at were the following:—

Reflection and Refraction.—A polished plate of glass was compared with the same glass in a finely powdered condition, care being taken that there was the same quantity of material on a unit of area. The radiograph of the powdered glass was about 3 per cent deeper than that of the polished plate. Hence reflection or refraction would appear not to have been entirely absent.

Solid or Liquid.—To determine whether the passage from a liquid to a solid condition affects the amount of absorption, experiments were made with paraffin in the two states. The result was practically the same in each case.

Combination or Mixture.—Pounded crystals of the double sulphate of copper and ammonium gave practically the same absorption as a mere mixture of the two constituent salts in a similar state of division. Hence the chemical union had no influence on the result.

Metal and Oxide.—Finely divided metallic copper was found to absorb about 2 per cent more rays than either the black oxide, CuO, or the red oxide, Cu_2O, when the depth of the mass penetrated contained the same amount of metal. It would appear from this as though the oxygen, instead of adding a little to the general result, as might have been expected, had the opposite effect. A similar result had been previously obtained when the comparison was made with sheet copper.

Change of Atomicity.—The above experiments showed also that the change of atomicity in these two oxides of copper did not produce any notable difference. The same result was also obtained when the two oxides of mercury, the red HgO, and the black Hg_2O, were similarly examined. A third instance of a like character was obtained with lead. The yellow litharge, PbO, and the puce coloured peroxide, PbO_2, were identical in their absorptions. Another experiment, to determine whether change of atomicity caused any difference, was made with ferrous and ferric oxalates, FeC_2O_4 and $Fe_2(C_2O_4)_3$. In order to form a comparison between the two, so much oxalic acid was added to the ferrous salt as was necessary to equalise the amount of carbon and oxygen in the two bodies. Again the result was almost identical.

Carbon and Hydrocarbons.—The former experiment on the absorption of carbon and various hydrocarbons was repeated with additional precautions, and varied as to length of exposure, distance from the radiating point, &c. The hydrocarbons were chosen so as to represent both crystalline and liquid substances, varying also in saturation from amyl hydride, which is a saturated compound, through turpentine, benzene, and naphthalene, to anthracene, the furthest removed from saturation. The depth of the substance penetrated always contained the same amount of carbon. In almost every instance the uncombined carbon was found to absorb a little more than the equivalent quantity of any of the hydrocarbons. The following table gives the final average results of a large number of comparisons, carbon always being taken at 100.

Carbon	Solid, black	C	100
Anthracene ..	,, white	$C_{14}H_{10}$	96
Naphthalene ..	,, ,,	$C_{10}H_8$	93
Amyl hydride ..	Liquid, colourless	C_5H_{12}	96·5
Turpentine ..	,, ,,	$C_{10}H_{16}$	95
Benzene	,, ,,	C_6H_6	94·5

Though the amount of hydrogen, and the consequent degree of saturation, is extremely various, there does not appear to be a correspondence in the variations of the power of absorbing the X rays; but the variations scarcely exceed the limit of error of experiment.

The experiments of this year therefore confirm the opinion previously expressed, that the absorption of the Röntgen rays by a compound body is almost wholly dependent upon the absorption exercised by its constituents. It is little, if at all, modified by their physical condition, or by change of atomicity, or by other differences of combination.

The question, however, forces itself on our minds, whether these small differences of results may not be due to the presence in the Röntgen radiations of small quantities of rays, which, though they have passed through aluminium foil, have properties somewhat analogous to ordinary light. It is evident that if a small amount of sunlight were to become mixed with the Röntgen rays it would increase the apparent absorption by the pounded glass, or by opaque metals, or black carbon. We venture to think that if such supposed rays could be entirely sifted away, the Röntgen radiations in their passage through a body would be affected merely by the nature of the atoms forming it, and that the law that the absorption by a compound is the mean of the absorption due to its several constituents would be not only proximately but absolutely true. The answer to this question must depend upon further research.

In some of the later experiments we have used a simple apparatus for testing the grade of the Röntgen rays employed. In a sheet of thick lead a rectangular window was cut, and over one-half of the window we fastened a piece of thin platinum or tin foil. An aluminium "stepped" scale was adjusted over the other half of the window, and the whole inserted between the radiating tube and an ordinary fluoroscope. On looking into the fluoroscope the rectangular window was seen as a patch of light, each half differently illuminated. But by sliding the aluminium scale to and fro, a position was found for it at which the two halves of the window became uniformly illuminated. The particular "step" of aluminium which was then in position was the index of the "grade" of the rays.

* Abstract of a Paper read before the British Association (Section B), Bristol Meeting, 1898.

Since this paper was read we find that Professor Röntgen has recently described a somewhat similar apparatus, the chief difference being that he brings many of the aluminium "steps" in view at the same time.

SOME RESEARCHES ON THE THERMAL PROPERTIES OF GASES AND LIQUIDS.*

By SYDNEY YOUNG, D.Sc., F.R.S.

Gases under moderate or low pressures are characterised by the simplicity of the laws relating to the variation of their volume with temperature and pressure. But when the pressure is greatly increased, these laws no longer hold good; at constant temperature the product pv, instead of remaining constant, diminishes until a minimum is reached, and at still higher pressures increases again, and this increase continues up to the highest pressures that have been reached.

A most important advance in the explanation of the behaviour of compressed gases and of liquids was made just twenty-five years ago by Van der Waals, who, taking into account the two facts (1) that the molecules of a gas attract one another, (2) that they occupy a finite volume, and are not mere mathematical points, proposed the formula—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

in place of the simple one $pv = RT$. The formula of Van der Waals expresses very well the general relations of pressure, temperature, and volume for both gases and liquids, but does not give the actual values with sufficient accuracy, and many attempts have been made to alter it in such a way as to bring about a better agreement. It is noticeable that at constant volume the formula becomes $p = KT - c$, where K and c are constants, depending on the volume, and this simple relation has been found to hold good for gases by Amagat, and for both gases and liquids by Ramsay and myself. Within the last few years I have investigated the behaviour of a hydrocarbon, isopentane (*Proc. Phys. Soc.*, xiii., p. 602), through a very wide range of volume (1·6–4000 c.c. per grm.), and of normal pentane through a smaller range, and the data so obtained have led Rose-Innes (*Proc. Phys. Soc.*, xv., p. 126; xvi., p. 11) to a formula—

$$p = \frac{RT}{v}\left\{1 + \frac{e}{v + k - gv^{-2}}\right\} - \frac{l}{v(v + k)},$$

based on the simple one $p = KT - c$, which reproduces the observed isothermals from the largest volume to about 3·4 c.c. per grm., with a maximum error of slightly over 1 per cent.

A complete investigation of this kind requires, however, a large amount of time, and can only be carried out with very stable substances of comparatively low critical temperatures, and it occurred to me about eleven years ago, that a careful study of certain generalisations, deduced by Van der Waals from his formula, might yield valuable results, and perhaps indicate the direction in which the formula requires alteration.

The generalisations may be stated thus:—If any two substances, A and B, are compared at pressures, P_A and P_B, proportional to their critical pressures, π_{OA} and π_{OB}, their boiling-points (absolute temperatures), T_A and T_B, will be proportional to their critical temperatures, θ_{OA} and θ_{OB}, and their volumes, both as liquid, V_A and V_B, and as saturated vapour v_A and v_B, will be proportional to their critical volumes, ϕ_{OA} and ϕ_{OB}. It would follow from this that at "corresponding" pressures the ratios of the actual to the theoretical density of saturated vapour, $\frac{D}{\overline{D}}$, should be the same for all substances.

It is convenient to speak of the ratio of the pressure to the critical pressure as the "reduced" pressure, π, the actual pressures, P_A, P_B, being called "corresponding" pressures.

I proposed, therefore, to determine the vapour pressures and the specific volumes (both as liquid and as saturated vapour) of a considerable number of substances from low temperatures to their critical points, and in the first place I chose some compounds of elements belonging to the same group in the periodic table, as it seemed possible that some points of interest might thus arise. The first substances I examined were the four monohaloid derivatives of benzene, as well as benzene itself (*Trans. Chem. Soc.*, lv., p. 486), and the result of the investigation was to show that, when the haloid derivatives are compared together, the generalisation, as regards temperature and pressure, hold good accurately; but there is this peculiarity about these compounds, that their critical pressures are equal, or very nearly so, and therefore "corresponding" pressures are in this case equal pressures. The critical pressure of benzene itself is different, and when the hydrocarbon is compared with any of its haloid derivatives, the differences between the temperature ratios are much greater. As regards the volume ratios, the differences are small in all cases.

The only other substances, bearing on the periodic arrangement of the elements, which have been yet examined are the tetrachlorides of carbon and tin (*Trans. Chem. Soc.*, lix., p. 911). The critical pressures differ considerably, and the relationship resembles that of the normal paraffins to each other, which will be referred to later. Many of the chlorides of the elements are very hygroscopic, and attack mercury at high temperatures, and it was thought better to postpone their further examination, and to obtain the data for a few series of homologous organic compounds. Up to the present, in addition to the three lowest alcohols, investigated by Ramsay and myself, ten esters (*Trans. Chem. Soc.*, lxiii., p. 1191) and four paraffins (*Ibid.*, lxvii., p. 1071; lxxi., p. 446; lxxiii., p. 675; *Proc. Phys. Soc.*, xiii., p. 602) have been studied, and with the exception of the alcohols, it has been observed in every case (and the same remark applies to the tetrachlorides of carbon and tin) that the ratios $\frac{T}{\theta_0}$ at any reduced pressure increase with rise of molecular weight. No definite relation is observable between the molecular weights and the ratios $\frac{V}{\phi_0}$ and $\frac{v}{\phi_0}$ in the case of the esters, but with the three normal paraffins (pentane, hexane, and heptane) and the two tetrachlorides, the ratios $\frac{v}{\phi_0}$ increase and $\frac{V}{\phi_0}$ diminish slightly with rise of molecular weight. With the alcohols, on the other hand, the ratios $\frac{T}{\theta_0}$ and $\frac{V}{\phi_0}$ are irregular and $\frac{v}{\phi_0}$ diminish.

Another point of interest is the comparison of isomeric compounds, but up to the present, the only two pairs of isomers investigated are methyl butyrate and isobutyrate, and normal and iso-pentane. In both cases there is a clear relationship between the ratios and the constitution, the normal and iso-compounds standing to each other in much the same relative positions as a higher and lower normal paraffin.

It is worthy of remark that the volumes of a grm. of all four paraffins are nearly the same (4·266–4·303) at the critical point.

Looking at the data for the twenty-six substances examined, it is evident that they may be divided into groups:—1. Benzene and its haloid derivatives, ether

* A Paper read before the British Association (Section B), Bristol Meeting, 1898.

the tetrachlorides, and the paraffins. 2. The ten esters. 3. The alcohols. 4. Acetic acid. The members of Group 1 may be regarded as normal; the deviations of the ratios from constancy are small, though, as pointed out, they exhibit certain regularities; in Group 2 the values of $\frac{v}{\phi_0}$ are rather higher, and of $\frac{V}{\phi_0}$ rather lower than in Group 1; in Group 3 the ratios $\frac{T}{\theta_0}$ and $\frac{v}{\phi_0}$ are very high; for acetic acid $\frac{T}{\theta_0}$ and $\frac{V}{\phi_0}$ are high, but $\frac{v}{\phi_0}$ very low. The marked differences between the alcohols and acetic acid, and the large deviations in both cases, are probably to be accounted for by the fact that the molecules of the alcohols at moderate temperatures are polymerised in the liquid—but not the gaseous—state, whilst with acetic acid there is polymerisation in both states.

The ratios $\frac{D}{D'}$ at the critical point should, according to Van der Waals, be the same for all substances, the molecules of which undergo no dissociation or polymerisation, and he gives the value of this ratio as $\frac{8}{3}$ or 2·6. Now the ratio depends on the constant b in the equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

and Van der Waals takes b to be four times the actual volume of the molecules in unit mass of substance; O. E. Meyer, however, contends that $b = 4 \times \sqrt{2}$ times the volume of the molecules, and it has been pointed out by Heilborn and by Guye that, if that is so, the ratio 2·6 should also be multiplied by $\sqrt{2}$, which would give the value 3·77. It is remarkable that the mean value for the twelve substances in Group 1 is 3·77, from which it may be concluded that the molecules of these substances in the critical state are simple like those of the gas. At the same time it is to be noticed that with the three normal paraffins and the two tetrachlorides $\frac{D}{D'}$ shows a slight increase with rise of molecular weight.

The ratios for the ten esters are a little higher (3·87 to 3·95); decidedly higher for the alcohols, especially methyl-alcohol (4·52—4·02), and much higher for acetic acid (5·00). It would appear from this that the molecules of the alcohols and acetic acid are polymerised to a considerable extent at the critical point, and this conclusion is supported by the generally abnormal behaviour of these substances, and agrees with that of Ramsay and Shields, that in the liquid state at moderate temperatures their molecules are decidedly complex, whilst those of the majority of the compounds examined by them are probably simple.

I hope to continue the investigation of the paraffins and other hydrocarbons in order to obtain further light on the points referred to, and it will be of interest to compare the molecular volumes at the critical points, and at a series of reduced pressures.

The accurate determination of the critical constants is a matter of great importance. It is best to employ an apparatus similar in principle to that of Andrews, in which the temperature, pressure, and volume can be altered at will; though the critical temperature may be determined with but small error in a sealed tube, if the quantity of liquid taken is such that its critical volume is approximately equal to the capacity of the tube. With a pure substance, free from air, two independent determinations of the critical temperature should certainly not differ by 0·1°, unless the temperature is above 300°, when the experimental difficulties are greater. The error in the determination of the critical pressure should not exceed 0·2 per cent, but the critical pressure is greatly affected by the presence of even very small quantities of impurity (and, of course, of air), and in comparing two specimens of the same substance, one of which is known to be pure, the agreement of the critical pressure is probably the most delicate test of the purity of the other.

The only method yet known by which the critical volumes can be accurately determined is the indirect one based on the "law of diameters" of Cailletet and Mathias. These physicists made the very important discovery that the mean densities of liquid and saturated vapour for any "normal" substance are a linear function of the temperature (or $D = D_0 - at$ where D = the mean density), and since, at the critical point, the two densities are equal—or rather there is only one—the value of D at that point gives the critical density, from which the critical volume is, of course, easily calculated. I have been able to show that the law of Cailletet and Mathias holds good with great accuracy right up to the critical point (with normal pentane observations were taken to within 0·05° of the critical temperature), for all the compounds examined except the alcohols. It has, in view of these results, been suggested, I think justly, by M. Guye, that a serious deviation from the law may be taken as a proof of the existence of molecular dissociation or polymerisation.

It is true that a few years ago I was under the impression that a direct determination of the critical volume was possible, and the values obtained do, indeed, bear as nearly constant ratio to the true critical volume, but they are about 14 per cent too low. The probable explanation of the error has been given by M. Gouy, who pointed out that, at the critical point, a substance is so extremely compressible, that in a long column the density increases very considerably from top to bottom, owing to the pressure exerted by the substance itself.

In the course of these researches ample proof has been obtained that the views of Andrews regarding the behaviour of a substance in the neighbourhood of the critical point are correct, and also that the vapour pressure of a pure substance is quite independent of the relative volumes of liquid and vapour. These points are referred to because they have been called in question by several observers during the last few years.

Two of the substances examined attack mercury at high temperatures, and it was therefore impossible to determine either their vapour pressures or specific volumes by the methods employed for the other liquids. The difficulty, as regards vapour pressure, was overcome by sealing a wider tube to the lower end of the volume tube, and using such a quantity of liquid that during the observations the lower end of the column was always in the wider and cold part of the tube. The height of the column of mercury in the tube must, under these conditions, be calculated (*Trans. Chem. Soc.*, lix., 917).

A method of determining the specific volumes of both liquid and saturated vapour in a sealed tube was also devised (*Ibid.*, lix., 37). When the specific volumes of the liquid are already known, this method, in a simplified form, is very convenient for determining the specific volumes of saturated vapour (*Ibid.*, lix., 125; *Proc. Phys. Soc.*, xiii., 617).

It is obviously necessary that, in order to obtain trustworthy results, pure substances must be employed, and, indeed, more time has been spent in the preparation of the pure substances than in the determination of their physical constants. The difficulties met with in the fractional distillation of liquids, more especially in the separation of pure hydrocarbons from petroleum, have led to an extended study of this subject, and both new apparatus (Chem. News, lxxi., 177; *Trans. Chem. Soc.*, lxxi., 440) and new methods of procedure (*Phil. Mag.*, 1894, p. 8) have been devised; it has thus been possible to separate perfectly pure normal and iso-pentane (B. P. 27·95° and 36·3°) from the complex mixture of hydrocarbons in American petroleum.

ACTION OF WATER AND SALINE SOLUTIONS ON METALLIC IRON.

By ROBERT MELDRUM, F.C.S.

Action of Water.

THE following experiments were made with the view of ascertaining whether the oxidation of pure iron takes place in chemically and biologically pure water; also if the general rule that iron is unacted upon by alkaline solutions holds good. The trials were made in 4-oz. stoppered bottles, free from lead. The distilled water was freshly prepared, and during the time under observation the trials were freely exposed to the light. Six feet of polished piano-wire, weighing 4·11 grms., was used in each experiment; it being made into a coil and fully immersed.

1. Town water, of 16° hardness, with about 25 c.c. air in bottle. In a few days the metal was coated with a yellow deposit, there being at the bottom a large yellow precipitate, the under layer of which was bluish black or very dark green.

2. Distilled water with about 25 c.c. of air. At the end of four weeks the wire became partly corroded; large precipitate at bottom, the lower part of which was bluish black, especially where it touched the metal, the upper portion being yellow.

3. Distilled water with bubble of air in bottle. In three weeks heavy yellow precipitate at bottom.

4. Distilled water with bubble of air. In four weeks the wire was dull; yellow precipitate at bottom, with shining transparent scales.

5. Distilled water, free from NH_3 and therefore CO_2, with air bubble. In a few weeks the iron was very dull; dirty yellow precipitate at bottom, intermixed with innumerable transparent scales.

6. Distilled water with about 15 c.c. of air. Wire coated with black tarnish; large brown precipitate at bottom, containing numerous shining scales. The glass was highly iridescent where it touched the metal.

7. Distilled water with no air bubble. Water became cloudy in ten minutes, yellow in one hour, and at the end of five hours there was an orange precipitate at the bottom.

8. Distilled water free from NH_3, and therefore CO_2, with air bubble in bottle. Iron corroded; yellow precipitate in three hours; little change in twenty-four hours.

9. Distilled water boiled in 4-oz. flask plugged with cotton wool, cooled, and charged with sterilised iron wire; half air and half water in flask. Water became yellow in twenty-four hours; large precipitate in several days; iron partly rusted.

10. Distilled water boiled for an hour in 8-oz. flask plugged with wool while boiling: when cold, put in bright sterilised wire. About 50 c.c. air in bottle. Wire rusted very slightly; no yellow deposit in four days.

11. Distilled water boiled for one hour in 8-oz. flask. Placed in wire and plugged with cotton wool during boiling. Wire rusted badly in twenty four hours; in several days, much yellow precipitate.

12. Distilled water boiled in 8-oz. flask. While still warm, placed wire in same; filled with boiling water to neck and corked, thus leaving no air bubble in flask. After four weeks the liquid was only slightly yellow, but no deposit on wire.

13. Distilled into stoppered bottle of 130 c.c. capacity until completely full NH_3, and therefore CO_2, free water. Placed therein six feet of wire; after placing, there remained in the bottle a very small air bubble. In four hours a yellow precipitate formed, and at the end of twenty days the air bubble had increased in size to about 1 c.c., the wire having become coated with black tarnish. The yellow precipitate had increased in volume, and contained both ferrous and ferric iron, and after ignition weighed 0·0115 grm., and when shaken innumerable small glistening iridescent scales appeared; the inside of the bottle was covered with iridescent lustre.

14. Same experiment as above, but with 12 feet of wire. Same results. This contained an excessive quantity of lustrous plates, some being of very large area. Weight of ignited deposit, 0·01 grm.

From the above experiments it will be seen that the oxidation of iron takes place in the absence of bacteria and other forms of life, NH_3, and CO_2. In the best of the experiments free O and N must have been present in the water, but to a very small extent; and, as yet, it is therefore an open question as to whether it is the water or dissolved oxygen which acts on the metal.

When a coil of tarnished or bright wire is placed in pure distilled, soft, hard, or any other kind of water, and exposed to light, the following is what usually takes place:—There is immediately formed a white cloud around the metal, which gradually increases until, in about fifteen minutes, the whole liquid becomes cloudy and then yellow, and in about three or four hours a yellow precipitate falls to the bottom. Wire, after immersion for several weeks, always appears to be slightly brittle, and possesses a smell of ozone. When the surface of iron exposed is great in proportion to the volume of water, and especially on free contact with the air, the bottles become internally coated with a film which communicates a highly iridescent lustre to the glass. The small glistening plates found among the hydrated oxides appear under the microscope to be detached parts of this transparent matter. Whether these films are due to bacteria, decomposition of the glass, or deposition of iron compounds I am unable to say.

Action of Saline Solutions.

In the following series of experiments the wire was immersed in the solution, the bottles being half-full of liquor. The substances were pure, and were all alkaline to phenolphthalein with the exception of sodium and potassium hydrogen phosphates.

Calcium Hydrate.— Saturated clear solution; wire quite bright at end of four weeks; no deposit.

One per cent Sodium Peroxide.—Wire quite bright at end of ten days; no deposit.

One per cent Sodium Hydrate.—Wire quite bright at end of four weeks; no action.

One per cent Potassium Hydrate.—Wire quite bright at end of four weeks.

One per cent Barium Hydrate.—No action in ten days.

One per cent Ammonium Hydrate.—Iron tarnished yellow in four weeks.

One per cent Sodium Carbonate.—Iron tarnished yellow in four weeks.

Five per cent Strontium Hydrate.—No action in four weeks.

One per cent Sodium Acid Carbonate. — Immediate action; dirty yellow precipitate in twelve hours. Iron turned black.

One per cent Sodium Biborate.—No action on metal in four weeks, but slight white sediment at bottom.

One per cent Sodium Hydrogen Phosphate.—A precipitate begins to form in fifteen minutes; large precipitate in twenty four hours.

One per cent Potassium Hydrogen Phosphate. — Same remarks as above.

One per cent Sodium Metaphosphate.—Wire covered with air bells in fifteen minutes, and slightly dull in four days. In ten days the upper portion of the solution is yellow, the lower portion green.

One per cent Sodium Pyrophosphate.—Immediate action; orange sediment in twelve hours; wire coated with deposit in six days.

One per cent Potassium Carbonate.—In six days large rust growth on metal, with a few particles at bottom.

One per cent Potassium Biborate.—Small white precipitate in ten days.

One per cent Potassium Borate.—In ten days a large rust growth on wire, but no precipitate.

It is clear from these experiments that all alkaline salts

do not prevent the oxidation of iron. It is remarkable that sodium peroxide should have no action, whereas potassium carbonate produced much. From this it appears that alkaline potassium salts act on iron to a much greater extent than those of sodium. The bicarbonates were decomposed very rapidly, with the formation of *large* white precipitates, eventually turning yellow.

ON THE

ANALYSIS OF MOLYBDENUM COMPOUNDS.

By HARRY BREARLEY.

I. *The Estimation of Molybdenum.*

Chatard's Process. — Chatard proposed to estimate molybdenum by adding lead acetate to the solution of an alkaline molybdate. The precipitated molybdate of lead, after washing and drying, is to be ignited—the paper separately—at a temperature not beyond a low red heat.

Chatard (Chemical News, xxiv., 175) illustrated the process by test analyses on a solution of pure soda molybdate, but does not mention whether the solution was acid or neutral. Fresenius ("Quant. Anal.," i., 289) mentions the process, but says that it is only applicable for solutions of *pure* alkaline molybdate.

Being in need of a reliable and simple process of esti mating molybdenum as separated from diverse metallurgical compounds, Chatard's, amongst others, was tried. As the early results were so promising, the general bearings of the method were worked out, and are here set down.

Starting with a solution of pure soda molybdate, it was found that from neutral solutions precipitation with neutral lead acetate was accurate, but that from very faintly alkaline solutions part of the excess of the precipitant is decomposed, though hardly noticeably so if—as Chatard points out — only a slight excess of acetate is used. In any case it is troublesome to have to perform operations in accurately neutralised solutions; the first step, therefore, was to determine whether the precipitation might not be made from a slightly acid solution.

In determining the influence of the following compounds, an amount of alkaline molybdate equivalent to 0·1 grm. molybdenum was used in every case. The figures given represent the amount of Mo recovered, and by their greater or less approximation they indicate the influence of the added compound.

Influence of Acetic Acid.—The lead molybdate, which from neutral solutions is rather granular, becomes more and more powdery as the acidity increases and tends the more to pass through the filter. This fact would probably impose a limit on the excess of acid which could be used. The volume of solution precipitated from was was always about 250 c.c.

2	5	10 c.c., 33 per cent acetic acid.
0·1000	0·0999	0·0998 Mo recovered.

All further precipitations were made from solutions containing about 2 c.c. of free acetic acid.

Excess of Lead Acetate.—If neutral solutions are adhered to the danger of large excesses of lead acetate, in case a faint alkalinity has been overlooked, is evident. In acid solutions no such precautions need be taken.

40	100 percentage excess $Pb\bar{A}_2$
0·1001	0·1000 Mo recovered.

The prolonged washing of the more powdery precipitates with pure hot water tends, in the later stages, to give opalescent washings. This difficulty is entirely overcome by washing with a solution of 1 c.c. $Pb\bar{A}_2$* in 500 c.c. of water just acidulated with acetic acid.

* Strength of $Pb\bar{A}_2$ solution = 7·896 grs. crystals per litre.

Igniting the Paper Separately.—By inference from the behaviour of lead sulphates it may have been concluded that the ignition of the $PbMoO_4$ apart from the paper was necessary.

As the separation always involves time, trouble, and with powdery precipitates some danger of loss, it was thought worth while to observe the error which comes of igniting the precipitate and paper together. Whether the paper and precipitate was previously dried in the water-bath, or folded wet and placed in a crucible at the mouth of a muffle, or separated according to Chatard's instructions, it made no matter; the results were always the same. But this much must be said:—If the more expeditious method of drying in front of the muffle be adopted, then the early ignition should be allowed to take place at the lowest temperature practicable, otherwise patches of the paper are imperfectly decarbonised, and the higher temperatures needed to complete the ignition are disallowed by the instability of the lead molybdate.

In order to determine whether lead molybdate could be reduced by carbonaceous matter, half a grm. of finely powdered wood charcoal was placed in the solution either before or after precipitating the $PbMoO_4$. The moist precipitate is thus intimately mixed with carbonaceous matter, and takes a considerable time to ignite. Three separate tests, after igniting to constant weight and correcting for the charcoal ash, gave 0·0993 gr. of molybbenum instead of 0·1000 gr.

Temperature of Ignition.—It should not be inferred that ignition at temperatures beyond the minimum employable are attended with disastrous results. For general technical purposes a long range of temperature is admissible.

This latter statement is founded on numerous experiments, all showing that prolonged ignition at high temperatures causes only a very slow decrease in the weight of $PbMoO_4$. The following is a typical case:—Ignited at a low red heat the weight of $PbMoO_4$ was 0·3685 gr. By gradually increasing the temperature it fell to 0·3675. By pushing the muffle to full redness—at which temperature soda carbonate in an adjacent crucible readily fused—the weight after ten minutes fell to 0·3665. After remaining at this temperature (850—900° C.) for six hours, the weight was only reduced to 0·3650—a loss altogether of just under 1 per cent.

Influence of Alkaline Salts.—The salts were formed in the soda molybdate solution by adding a measured quantity of strong acid, neutralising with soda carbonate or ammonium hydrate as the required salt demanded.

	5 c.c.	10 c.c. acid used.
Soda chloride	0·1000	0·0998
,, nitrate	0·1001	0·1004
Ammon. nitrate	0·1003	0·1001
,, chloride	0·0998	0·0999

With the non-volatile salts great care was taken to eliminate possible compensatory errors. Unlike many precipitates, particularly gelatinous and flocky ones, the lead molybdate does not appear to hold associated alkaline salts very tenaciously. Thus we found that prolonged washings gave the same results as only three or four washings, and, to further confirm this observation, we have frequently re-dissolved the ignited $PbMoO_4$ in dilute hydrochloric acid, neutralised with ammonia, added an excess of acetic acid, a few more drops of lead acetate, and repeated the whole operation. This second precipitation never sensibly altered the result. In observing the influence of a series of metallic compound I have had regular occasion to make use of this repeated precipitation, chiefly for confirmatory purposes, but occasionally on account of the purifying nature of the process. We shall refer to it subsequently merely as re-precipitating the lead molybdate.

Ammonium acetate, of such strength as is obtained by neutralising 0·880 ammonia with 33 per cent acetic acid,

will be seen later to be an important reagent. Its influence in large quantities was therefore noted.

10 c.c.	30 c.c. ammon. acetate.
0·1000	0·1002 Mo recovered.

Like acetic acid it causes the precipitate to be powdery. With the larger amounts the filtrate needs re-passing through the pore-clogged paper.

It must be admitted that, in comparison with other processes, the behaviour of Chatard's under other than ideal circumstances is very satisfactory, and that, the above results being accepted, it should no longer be regarded as a process available only for the estimation of molybdenum in pure alkaline molybdates.

At this point we were satisfied that Chatard's process would meet our requirements, but—partly from curiosity, and partly, if possible, to avoid the separating of associated metals in some molybdenum alloys which occasionally engage us—we decided to observe the interference which the presence of some of the commoner metals would introduce. This kind of work is somewhat monotonous. We are of opinion, however, and we are supported in this alike by observation and experience, that one knows a method well only when he knows its limitations. Those limitations once determined, the knowledge serves the double purpose of minimising the danger of error and of eliminating a number of separations which, not uncommonly, introduce greater errors than they obviate.

The Interference of some Metals.

Attempts have been made to precipitate lead molybdate in the separate presence of about twenty metals. For the sake of brevity these may be treated of in classes.

First are those which exert no practical interference, and occasion no trouble beyond more careful washing or a re-precipitation of ignited $PbMoO_4$. These, and the results obtained with them are set forth in—

Table I.

Interfering metal.	Grm. added. 0·10	0·20
Manganese	0·1003	0·1003
Copper	0·0999	0·1001
Cobalt	0·1004	0·1001
Nickel	0·1003	0·1004
Zinc	0·1004	0 0999
Magnesium	0·1002	0·1009
Mercury (ic)	0·0999	0·1000
Uranium	0·1017	0·1015

The figures given are those obtained from the first precipitation of the lead molybdate. In every case the $PbMoO_4$ was re-precipitated, whether there was cause to suspect impurity or not.

Manganese and Copper.—The colour of pure lead molybdate (ignited) is creamy. Any compound then whose oxide is dark coloured is at once indicated. From the presence of manganese the ignited precipitate is darkened; but on treating with nitric acid and lead peroxide, so as to convert the Mn_3O_4 into permanganate, only a very faint colouration was observable. A similar remark applies to copper.

Cobalt.—Precipitates formed in cobalt solutions are greyish when ignited. On re-dissolving in strong HCl the traces of Co form a green solution. The colour disappears on diluting. I have found this reaction with cobalt and strong HCl to indicate as small an amount as 0·00005 grm. cobalt. After being purified by re-precipitation the $PbMoO_4$ rarely contains more than that negligible amounts.

This colour test could probably be used to indicate the extent to which a precipitate was contaminated with cobalt, in the same way as traces of iron are estimated by the sulphocyanide colouration. My experience has shown that only such amounts of cobalt are associated with the first precipitation of the lead molybdate as would pass unnoticed if it were not for the strong grey colour which the cobalt imparts to the precipitate.

It is impossible to wash *all* the cobalt from the first precipitate. Smith and Bradbury (*Berichte*, xxiv., 2930) have pointed out that cobalt forms a small quantity of a bluish-white precipitate in concentrated solutions of sodium molybdate; the fact that the moist precipitate has a *very faint* purple cast indicates that such a compound may be responsible for the greyness of the ignited $PbMoO_4$. The further fact that the greyest of the precipitates never weighed appreciably more than it should supports this view.

Nickel and Zinc.—On neutralising the acid solution of zinc and molybdenum a precipitate is formed. The usual excess of acetic acid mainly dissolves this precipitate, but a faint cloudiness—probably a molybate of zinc—remains. We find it to be perfectly safe to disregard this appearance so long as it is not more than an opalescence, if the lead acetate be added in excess to the cold solution. If the cloudiness is considerable the neutralisation is stopped short, and the remaining free HCl decomposed with ammonium acetate. Nickel exhibits this cloudiness in a lesser degree.

Mercury and Uranium.—A precipitate forms before neutralisation is effected. In the case of mercury it is dissolved slowly on heating with the excess of acetic acid; but in the case of uranium it is only slowly, if at all, effected by such treatment. In either case the warm solution immediately clears on adding ammonium acetate.

Uranium is the only element in Table I. which contaminates the precipated lead molybdate to any serious extent. The ignited precipitates are always yellowish-brown, and on treating with hydrochloric acid the colouring is at once dissolved. By re-precipitating the error may be reduced to half per cent, but the $PbMoO_4$ needs repeatedly precipitating to separate the last traces of uranium.

Volumetric Processes.

Molybdenum may be estimated indirectly by adding an excess of lead acetate, filtering off the lead molybdate, and applying to the filtrate any of the trustworthy methods of determining lead.

The determination of the lead by means of potassium chromate and ferrous sulphate (*Journ. Am. Chem. Soc.*, Nov., 1895) has given good results, but it needs careful working. All things considered this is not so rapid as the previously described gravimetric one, and is certainly much less delicate.

Schindler (Chemical News, lviii., 61) has described a volumetric process for the estimation of molybdenum in which lead acetate is added to an acidified solution of a molybdate until the latter ceases to give any colouration when mixed on a white-cupped tile with tannin.

We have experimented with this method on solutions of pure alkaline molybdates, and can readily aver that it gives rapid and approximate results. As the end of the reaction is approached the indications are rather uncertain.

It has been said that, in neutral or faintly acid (acetic) solutions, the precipitated lead molybdate is granular and easily filterable. In using Schindler's method we support or correct its conclusions in the following manner:—

Add lead acetate and use the tannin reaction as long as it is available. The degree of accuracy thus obtainable will vary little more than 1 per cent from the truth. Pour a little of the hot solution through a ribbed paper, and test the filtrate first with lead acetate, and if necessary with soda molybdate. Generally the first test will show that some molybdenum is still unprecipitated, and the intensity of the cloudiness, after a little experience, indicates approximately how much. The one or the other reagent is added as required, and the solution tested in this way until with absolute certainty it can be said that

neither soda molybdate nor lead acetate is present in other than negligible quantities. As the solution is passed and repassed through the same filter until the end is reached, there is no loss through the absorption of the paper. And, finally, it is always open, if desired, to complete the gravimetric operation.

This process is shorter than the gravimetric one, and on pure solutions it is equally accurate. We have not observed the interference of large amounts of metallic salts.

The test proposed as a supplement to Schindler's is a very delicate one. In a faintly but decidedly acid (acetic) solution, measuring 400 c.c., a distinct cloudiness is formed by lead acetate when only 0·0001 grm. of Mo is present,—that is, one part in four million parts of solution, a degree of accuracy not to be surpassed by the most fastidious working of the gravimetric process.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month all were found to be clear, bright, and well filtered.

The serious deficiency in the rainfall still continues. Rain fell at Oxford on six days only during September, the total fall being only 0·38 inch. The thirty years' average is 2·43 inches; we thus have a deficiency of 2·05 inches, bringing the total deficiency for the year up to 8·22 inches.

Our bacteriological examinations of 258 samples have given the results recorded in the following table; we have also examined 39 other samples, from special wells, standpipes, &c., making a total of 297 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	485
New River, filtered (mean of 26 samples) ..	12
Thames, unfiltered (mean of 26 samples) ..	2957
Thames water, from the clear water wells of five Thames-derived supplies (mean of 128 samples)	32
Ditto ditto .. .. highest	612
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	3378
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	27

Our bacteriological examinations of the 297 samples have been quite satisfactory. The extraordinary deficiency in the rainfall in the Thames Valley, which now amounts to 44·5 per cent from the 1st of January, as our tables show, has had no effect in causing deterioration in the water supply of the Metropolis.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE ACTION OF LIGHT UPON DYED COLOURS.*

(Continued from p. 193).

BLACK COLOURING MATTERS.

CLASS I.—VERY FUGITIVE COLOURS. (WOOL).

Azo Colours.

Wool Book XIV.

Acid Colours.—

4. Violet Black. From *p*-phenylene-diamine, with α-naphthylamine and α-naphthol-sulphonic acid NW. S. and J. III. 502.

Direct Cotton Colours.—

1. Nyanza Black B. From *p*-phenylene-diamine-azo-α-naphthylamine and amido-naphthol-sulphonic acid γ.
2. Tabora Black R. Constitution not published.

NOTES.—During the first "fading period" Violet Black changes to a dull vinous red colour.

CLASS II.—FUGITIVE COLOURS. (WOOL).

Azo Colours.

Wool Book XIV.

Acid Colours.—

6. Azo Nigrine R. From phenol-disulphonic-acid-azo-α-naphthylamine and β-naphthol.
12. Wool Black. From amido-azo-benzene-disulphonic acid and *p*-tolyl-β-naphthylamine. S. and J. III. 139.
13. Jet Black G. Constitution not published.
19. Phenylene Black. From α-naphthylamine-disulphonic-acid-azo-α naphthylamine and diphenyl-*m*-phenylene-diamine. S. and J. III. 152.
21. Anthracite Black R. From α-naphthylamine-disulphonic acid and α-naphthylamine-azo-diphenyl-*m*-phenylne diamine.
26. Azo Acid Black B. Constitution not published.
27. Azo Acid Black G. Constitution not published.

Direct Cotton Colours.—

10. Direct Deep Black T. Constitution not published.
11. Columbia Black 2B. Constitution not published.
12. Columbia Black B. Constitution not published.
13. Oxy Diamine Black N. Constitution not published.
14. Union Black S. Constitution not published.
16. Oxy Diamine Black SOOO. Constitution not published.
18. Columbia Black R. Constitution not published.

Direct Cotton Colours Developed.—

1. Diamine Black BH. From benzidine and γ-amido-naphthol-sulphonic acid and amido-naphthol-disulphonic acid H. Developed with Fast Blue Developer AD.
2. Diazo Black B. From benzidine and α-naphthyl-amine-sulphonic acid L. Developed with β-naphthol.

* Report of Committee, consisting of Dr. T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Bristol Meeting, 1898.

*3. Diamine Black ROO. From benzidine and β-amido-naphthol-sulphonic acid. Developed with Fast Blue Developer AD. S. and J. III. 187.
4. Diazo Black R. Constitution not published. Developed with β-naphthol.
5. Diazo Black H. Constitution not published. Developed with β-naphthol.
*8. Diamine Black BO. From ethoxy-benzidine and amido-naphthol-sulphonic acid γ. Developed with Fast Blue Developer AD. S. and J. III. 229.

Oxazine Colours.

Basic Colours.—
1. Cotton Black. Constitution not published.

Natural Colouring Matters.

Mordant Colours.—
Limawood (Fe). Cæsalpinia echinata (wood).

NOTES.—The following colours acquire a reddish or purplish tint during the fading process:—Azo Acid Blacks B and G, Columbia Blacks B and R, Union Black S, Oxy-diamine Black SOOO, Diamine Black RO and BO. An olive tint is acquired by Direct Deep Black T.

(To be continued).

TRANSFORMATION OF CHEMICAL ENERGY INTO ELECTRIC ENERGY.*

By Prof. F. FOERSTER.

(Concluded from p. 192).

THE original construction of the Borchers cell presented a series of defects which became more and more marked after prolonged use. We cannot here go into the details of the research which Borchers undertook in the endeavour to eliminate these defects, however useful they may have been to future workers on the subject. The greatest difficulty was to succeed in getting as perfect a contact as possible between the gas, the electrolyte, and the electrode, without allowing the solutions charged with the two gases to become mixed. The best results were obtained by stopping the continued current of air and by using an oxidising material which would be periodically regenerated by the atmospheric air. As an oxidising material Borchers took Weldon mud (manganite of lime mixed with a solution of chloride of lime). This mud is placed in an iron or lead box, which at the same time serves as an electrode; a flattened cell of refractory clay kept away from the air is plunged into the mud. This cell contains a horizontal plate of carbon which also serves as an electrode, and an acid solution of chloride of copper, through which a current of carbonic oxide is passed. The battery lasts until all the binoxide of manganese is reduced to the state of oxide. This can then be easily regenerated by blowing in more air. If we take precautions to maintain the solution of the chloride of copper, acid, and that of the manganite alkaline, the working of the cell will be very regular, and its electromotive force 0·6 volt with an external resistance of about 50 ohms. Borchers himself is far from wishing to attribute any commercial value to his cell, such as it is described. The question as to how far the oxidation of the carbonic oxide can be pushed in such a cell has not yet been decided. But it may be permissible to regard Borcher's process as a method for the preparation of oxalic acid, starting from carbonic oxide, a method which at the same time produces electric energy, and which therefore may some day lead to the solution of the problem. The researches of Borchers took place in the laboratory of Prof. Nernst at Gottingen, and in that of the Elberfelder Farbenfabriken.

A comparison of Borcher's experiments with those of Reed (*Zeit. f. Elect.*, iii., p. 87) will show us what different lines have been followed in the endeavour to construct a commercial galvanic battery. Reed based his research on the following fact. Sulphurous acid reacts on sulphuretted hydrogen, giving rise to the formation of water and sulphur. This reaction is followed by a disengagement of electric energy when carried out in a suitable apparatus constructed on the principle of a gas cell.

As for the two gases they are obtained in the following manner. Sulphur is burnt in a retort to produce sulphurous acid, which is passed into the cell; the heat given off by this combustion is sufficient to vapourise the sulphur and make the carbons which are in the retort red-hot. The vapour of the sulphur gives sulphide of carbon, which is mixed while hot with steam, giving rise to the following decomposition:—$CS_2+2H_2O=2H_2S+CO_2$. The sulphuretted hydrogen and the carbonic acid pass into the other compartment of the cell, where the electric current is generated by the reaction—$2H_2S+SO_2=3S+2H_2O$. We thus see that the three atoms of sulphur which were necessary to produce one molecule of sulphuretted hydrogen and one molecule of sulphurous acid are regenerated, and that the final result of all these operations is the transformation of the carbon into carbonic acid by the intermediary of sulphide of carbon. As the transformation of carbon into carbonic acid gives off 97,000 calories, and as the reaction between the sulphuretted hydrogen and the sulphurous acid gives off 25,000 calories, we see that 61 per cent of the heat of combustion is disposable for being transformed into electric energy.

From the above data Reed estimates the electromotive force of his cell at 0·63 volt. His apparatus, however, only gave him 0·36 volt. This disagreement may be partly explained by the fact that calculations of electric energy based on thermochemical data are never very exact. According to Reed the importance of his process consists less in its practical value than in its principle. He believes that the true method of obtaining the electric energy of carbon will be to employ an intermediary material which, like sulphur, would serve to make the oxidation of the carbon indirect. But in the presence of the results he obtained this assertion would appear to be a little pretentious.

We can see that the problem of making a carbon battery is still far from being solved. But it is possible that the solution of the more general problem of the commercial transformation of chemical into electric energy may be elucidated by the aid of other chemical reactions besides the combustion of the carbon. Several interesting researches have already been made in this direction.

We know that a cell with carbon electrodes, one of which is placed in a solution of chloride of protoxide of copper and the other in chloride of cupric oxide, gives an electric current when we pass chlorine gas through the cupric chloride; the current lasts as long as any unoxidised chloride of the protoxide remains. If this can be continually reproduced by means of a reducing gas we should get a practically continuous galvanic cell.

Andrews found (*Zeit. f. Elect.*, iii., p. 88) that sulphurous acid (but not carbonic oxide) can be used for this purpose. The sulphurous acid is transformed into sulphuric acid, and it is evident that it is the oxidation of the sulphurous acid which causes the electric energy of the cell.

No doubt it is now impossible to commercially isolate the sulphuric acid which is formed in this process; but we can do away with the copper salts if instead we use carbon tubes plunged into dilute sulphuric acid, and if by means of these tubes we introduce chlorine and sulphurous acid under high pressure.

The following reaction here serves for the production of electric energy—

$$SO_2+2H_2O+Cl_2 = H_2SO_4+2HCl,$$

and we obtain an electromotive force of 0·5 volt when the circuit is closed through a resistance of 1 ohm. It now remains to find a means of replacing the chlorine by the

* *Moniteur Scientifique*, Series 4, vol. xii., July, 1898.

oxygen in the air, so as to produce simultaneously pure sulphuric acid as well as electric energy.

As far as we can judge at the present day the formation of hydrochloric acid from its elements would still be the easiest reaction to employ for the production of electric energy by chemical means. The more the electrolytic manufacture of the alkalis progresses the more important becomes the question of the utilisation of the chlorine set at liberty in these electric processes.

While in the old Leblanc process the chlorine was considered as a valuable secondary product which could be produced in large quantities, it becomes in the electrolytic processes an encumbrance if we cannot find new applications for it. In the earlier times there was generally produced one ton of chloride of lime for each two or three tons of caustic soda, while the chlorine given off in the manufacture of the same quantity of soda by the electrolytic process gives nearly five tons of chloride. It is probable that a corresponding increase in the consumption of chloride of lime for bleaching purposes, disinfection, &c., is very unlikely. On the other hand, the electrolysis of the alkaline chlorides gives at the cathodes equivalent quantities of hydrogen, the utilisation of which is yet an interesting problem. The idea of combining the chlorine and the hydrogen naturally presents itself for the purpose of obtaining hydrochloric acid, of which the Leblanc process is at present the principal source.

The preparation of hydrochloric acid from chlorine and hydrogen has already been the subject of many patents, all of which point to the direct union of the two gases one with the other; but it is evident that we thus lose chemical energy which might be transformed into electricity if we could but construct a suitable apparatus in which the two gases could be combined indirectly. The energy that could be collected in this manner is fairly considerable, since the galvanic combination, Cl, ClH, H, gives with a great external resistance an electromotive force of 1·37 volts. If we could only succeed in making a commercial battery of this type the future of electrolytic processes for the manufacture of soda would be assured, even in face of the Solvay process. Thus by retransforming a part of the gas given off as hydrochloric acid we should obtain the electric current as a secondary product. The remainder of the chlorine would be converted into chloride of lime, while the corresponding quantity of hydrogen could, if advisable, be compressed.

These considerations naturally give many points for elucidation, but they show that the problem of the transformation of chemical into electrical energy can be attacked from more than one side.

THE IODOMETRIC DETERMINATION OF MOLYBDENUM.*

By F. A. GOOCH and JOHN T. NORTON, Jun.

A PROCESS for the iodometric determination of molybdic acid, which consists in treating a soluble molybdate in a Bunsen distillation-apparatus with potassium iodide and hydrochloric acid, has been advocated by Friedheim and Euler (*Ber. d. D. Chem. Gesell.*, xxviii., 2066). According to this process the molybdate, containing from 0·2 grm. to 0·3 grm. of molybdenum trioxide, is treated with from 0·5 grm. to 0·75 grm. of potassium iodide, and enough hydrochloric acid, of sp. gr. 1·12, to fill two-thirds of the flask of the apparatus. The liquid is warmed until heavy vapours of iodine fill the flask, and then boiled until iodine vapour is no longer visible and the colour of the liquid residue is a clear green. The iodine liberated is collected in the distillate and titrated with sodium thiosulphate, every atom of iodine found indicating presumably the reduction of a molecule of molybdic acid to the condition of the pentoxide Mo_2O_5,

It was pointed out in a former article from this laboratory (Gooch and Fairbanks, *Amer. Journ. Sci.*, IV., ii., 156), that greater precaution than was taken by Friedheim and Euler is necessary in order that the reduction may proceed according to theory, and that the iodine collected may serve as a reliable measure of the molybdic acid. It was found that the green colour of the liquid comes gradually, and that it may develop distinctly before the molybdic acid is fully reduced. It was found, also, that since even a trace of oxygen liberates iodine from the hot mixture of potassium iodide and hydrochloric acid of the strength employed, it is not sufficient to rely upon the volatilisation of iodine to expel the air originally in the apparatus, but that it is essential to conduct the distillation in an atmosphere devoid of oxygen. The suggestion was made, therefore, that the operation should be carried on in a current of carbon dioxide, and that the mixture, constituted definitely, should be boiled between stated limits of concentration which were determined by experiment. It was found that when amounts of a soluble molybdate containing less than 0·3 grm. of molybdenum trioxide are treated with potassium iodide, not exceeding the theoretical proportion by more than 0·5 grm., and 40 c.m.³ of a mixture of the strongest hydrochloric acid and water in equal parts, the reduction proceeds with a fair degree of regularity, and is practically complete when the volume has diminished to 25 c.m.³ If the operation is properly conducted in an atmosphere of carbon dioxide, it was shown that the iodine in the distillate may be trusted to indicate the molybdic acid within reasonable limits of accuracy. It appeared, however, that too great an excess of potassium iodide tends to induce excessive reduction, and that the same tendency shows when the liquid is concentrated to too low a limit.

To this criticism Friedheim took exception (*Ber. d. D. Chem. Gesell.*, xxix., 2981), and contrasted, to their disadvantage, our results by the modified method with those of Friedheim and Euler by the original method. It became necessary, therefore, to point out (Gooch, *Amer. Journ. Sci.*, IV., iii., 237) the fact that of the results published by Friedheim and Euler, upon which reliance was placed to prove the liability of their method, five out of seven in one series and one out of five in another series had been calculated incorrectly from data given. Another series of six determinations was, however, apparently faultless in this respect. More recently (*Zeit. f. Anorg. Chem.*, xv., 454) Euler has explained that the errors were not really arithmetical. Two of them may be presumed, inferentially, to be due to careless copying or proof-reading; and four, we are told by Euler, were introduced into the series by mistake, and actually represent (as Prof. Friedheim kindly informs him) the analysis of a sample of ammonium molybdate of undetermined constitution,—that is to say, the figures now given by Euler represent the original percentages of molybdenum trioxide which had been changed by some unconscious process from—

80·62	per cent to	81·85 per cent.
80·71	,,	81·69 ,,
80·63	,,	81·66 ,,
80·78	,,	81·78 ,,

Curiously enough Euler's corrected figures, as given here, are still affected by trifling arithmetical errors of from one to four units in the second decimal place. The agreement of these results among themselves is no proof of the correctness of the process of analysis. The great variation between the average percentage of molybdenum trioxide in ammonium molybdate as found by Euler in a molybdate of known constitution, and the percentage of the trioxide as found by Friedheim (if we understand Euler aright), may be due conceivably to either or both of two causes, viz., the change of material analysed and the change of operator or conduct of the operation. We shall show in

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vi., 1898.

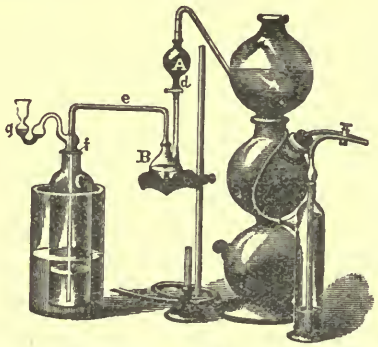
the following account of our work that the exact control of the conditions of treatment, along the lines laid down formerly, is actually essential to the reduction of molybdic acid according to the theory of the process.

Our experiments were made with ammonium molybdate twice re-crystallised from the presumably pure salt. The constitution of the preparation was determined by careful ignition *per se*, and, for greater security, with sodium tungstate free from carbonate. It contained 81·83 per cent of molybdenum trioxide.

The potassium iodide which we used was prepared by acting with re-sublimed iodine upon iron wire, and precipitating by potassium carbonate—the proportions of iodine and iron having been adjusted to secure the formation of the hydrous magnetic oxide of iron. The filtrate from the iron hydroxide gave on evaporation and crytallisation potassium iodide which was free from iodate.

The hydrochloric acid was taken of sp. gr. 1·12, because this is the strength used by Friedheim and Euler.

The sodium thiosulphate employed was taken in nearly decinormal solution, and was standardised by running it into an approximately decinormal solution of iodine which had been determined by comparison with decinormal arsenious acid made from carefully re-sublimed arsenious oxide. We chose this method of standardising—the introduction of the thiosulphate into the iodine—rather than the reverse operation, in order that the conditions of the actual analysis might be followed in the standardisation.



The distillation apparatus was constructed with sealed or ground joints of glass wherever contact with iodine was a possibility. It was made by sealing together a separating funnel A, a 100 c.m.³ Voit flask B, a Drexel wash-bottle C, and a bulbed trap *g*, as shown in the figure. Upon the side of the distillation-flask B was pasted a graduated scale by means of which the volume of the liquid within the flask might be known at any time. Carbon dioxide, generated in a Kipp apparatus by the action of dilute hydrochloric acid (carrying in solution cuprous chloride to take up free oxygen) upon marble previously boiled in water, was passed through the apparatus before and during the operation, so that it was possible to interrupt the process of boiling at any point of concentration, to remove the receiver by easy manipulation, to replace the receiver, and to continue the distillation without danger of admitting air to the distillation flask.

In experiments to be described—(1) to (5) of the table—the proportions of potassium iodide and molybdic acid, and the strength of the hydrochloric acid recommended by Friedheim and Euler were retained. The essential change of condition is the removal of atmospheric air from the distillation flask before the acid is admitted to contact with the other reagents. Potassium iodide (3 grm.) and water (200 c.m.³) were put into the receiver C, and a little of this solution was allowed to flow into the trap *g*. Ammonium molybdate carefully weighed (0·3 grm.) and potassium iodide (0·5 grm. to 0·75 grm.) were introduced into the distillation-flask B, the apparatus was connected as shown in the figure and carbon dioxide was passed freely through the whole apparatus for some minutes. The stop-cock *d*, between the bulb of the funnel A and the flask B, was closed and hydrochloric acid (40 c.m.³, sp. gr. 1·12) was poured into the funnel; the air above the liquid in the funnel was displaced by carbon dioxide through the space between the neck of the funnel and the loosely adjusted stopper carrying the inlet tube; the connection between the funnel and inlet tube was tightened, the stop-cock opened, and the acid, under the pressure of carbon dioxide, was permitted to flow into the flask. In this way the acid, iodide, and molybdate were made to interact with little danger of the presence of oxygen. The flask was heated by the Bunsen burner and the iodine evolved, passing over quietly in the slow current of carbon dioxide, collected in the receiver. The liquid was boiled until fumes of iodine were no longer visible above the liquid in the flask and connecting tubes backed by a ground of white, and then a full minute more. At this stage, the green colour of the liquid having developed fully, the apparatus was permitted to cool, the current of carbon dioxide was increased, the cap of the receiver was loosened at *f*, the contents of the trap were washed back into the receiver, the rest of the apparatus was lifted bodily from the receiver, the liquid adhering to the inlet tube was washed off into the receiver, and the end of the tube was dipped immediately into a solution of potassium iodide. The constant flow of carbon dioxide prevented reflux of air during the transfer, and as soon as the end of the tube had been submerged in the solution of potassium iodide (which was employed not only as a water-seal, but to catch any iodine still carried in the gas), it was possible to reduce the rapidity of the current.

After titrating the iodine in the distillate the receiver was again placed in the train and the process of distillation was resumed under the former conditions and continued until the volume of the liquid, as indicated upon the scale, had diminished to 25 c.m.³, when the distillation was interrupted. The apparatus was manipulated as before to prevent access of air, and the iodine evolved in the second treatment determined. A third period of distillation served to show the iodine liberated during the concentration of the liquid from 25 c.m.³ to 10 c.m.³

(To be continued).

MISCELLANEOUS.

Salts of Pertungstic and Permolybdic Acids.—P. Melikoff and L. Pissarjewsky. — To prepare these salts solutions of sodium and potassium hypotungstates and hypomolybdates are cooled to −2°, and added to the calculated quantity of H_2O_2; on addition of alcohol cooled to −12°, precipitation takes place. The precipitate is kept for some time at −12°, and then filtered and washed with alcohol. It can then be dried on a porous tile and analysed. The salts prepared by this method have the following compositions:—

$Na_2O_2.WO_4.H_2O_2+(Na_2O_2)_2WO_4+7H_2O$
$Na_2O_2.WO_4.H_2O_2$
$K_2O_4.WO_4.H_2O$
$K_2O_2.MoO_3.H_2O_2$.

All these salts are very unstable, and are decomposed by water, with evolution of oxygen. To analyse the salts a weighed quantity of the salt is decomposed by dilute H_2SO_4 at −6°, and the liberated oxygen titrated with permanganate solution.—*Ber. der Deutsch. Chem. Gesell.*, 1898, No. 6.

MEETINGS FOR THE WEEK.

FRIDAY, 28th.—Physical, 5. "An Influence Machine," by W. R. Pidgeon, M.A. "The Repetition of an Experiment on the Magneto-optic Phenomenon Discovered by Righi," by Prof. Silvanus P. Thompson, F.R.S. "The Magnetic Fluxes in Meters and other Electrical Instruments," by Albert Campbell, B.A.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2031.

NOTE ON THE INTERACTION OF SODIUM ARSENITE AND SODIUM THIOSULPHATE.*

By L. W. McCAY.

In the Chemical News for March 25th, 1898 (vol. lxxvii., p. 131), there is a note by Dr. Leonard Dobbin in which he calls attention to a new and interesting reaction which takes place when concentrated aqueous solutions of a cyanide and a thiosulphate are mixed and allowed to stand. The products formed are a thiocyanate and a sulphite :—

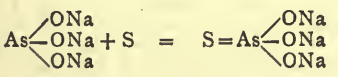
$$KCN + K_2S_2O_3 = CNSK + K_2SO_3.$$

This reaction of Dr. Dobbin is in some respects similar to one I discovered in the summer of 1897. By means of my reaction I have been able to prepare the tertiary sodium salt of orthomonothioxyarsenic acid in large amounts and in beautiful well-defined crystals.

I simply rub up in a mortar, with a sufficient quantity of caustic soda solution to form a thick paste, the calculated amounts of sodium arsenite and sodium thiosulphate. The reaction proceeds as follows :—

$$Na_3AsO_3 + Na_2S_2O_3 = Na_3AsO_3S + Na_2SO_3.$$

An atom of sulphur leaves the thiosulphate molecule and attaches itself *directly* to the arsenic atom of the arsenite molecule (*Chemiker Zeitung*, 1896, xx., No. 75) :—

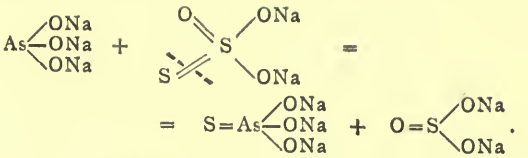


The paste is dissolved in water, the solution filtered, and from the filtrate the salt obtained by crystallisation. It is readily purified by one or two subsequent crystallisations from water.

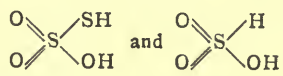
	Calculated for $Na_3AsO_3S + 12H_2O$.	Found for $Na_3AsO_3S + 12H_2O$.
Na_3	15·70 per cent	15·94 per cent
S	7·28 ,,	7·30 ,,
As	17·05 ,,	17·06 ,,

It may be well to state, however, that I am not in the habit of making use of this reaction for preparing the orthomonothioxyarseniates. The sodium compound is most easily and rapidly obtained by rubbing up in a mortar, with enough water to form a paste, the stöchiometrical amounts of *sulphur*, caustic soda, and arsenious oxide, dissolving the resulting mass in water, filtering the solution, concentrating it, and allowing the salt to crystallise out. A few c.c. of absolute alcohol added to the contents of the mortar serve to accelerate the reaction in a very marked manner. It will be seen that this latter method is but a modification of that of Weinland and Rumpf. It is, however, simpler and quicker than their original method, and, as far as yield is concerned, leaves nothing to be desired.

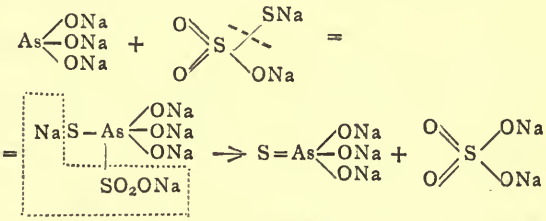
It was this method for preparing $Na_3AsO_3S + 12H_2O$ which suggested to me the use of sodium thiosulphate. As is well known, $Na_2S_2O_3$ yields sulphur very readily, especially when used for fusion purposes. The mechanism of the reaction is undoubtedly complicated. The simplest interpretation would be this :—



Since, however, the reactions of organic chemistry point to—



as representing the constitutions of thiosulphuric and sulphurous acids, such a simple interpretation cannot be held. If we assume the momentary existence of a complex intermediate compound, the reaction might be represented in this way:—



I am indebted to my friend Mr. Fred Neher for this suggestion.

Princeton, New Jersey, U.S.A.

* Received August 2, 1898.

ACTION OF WATER ON METALLIC COPPER AND LEAD.

By ROBERT MELDRUM, F.C.S.

Action on Copper.

The results obtained are expressed in parts per 100,000. The experiments were made in large test-tubes, each containing 100 c.c. of water and 7 feet bright copper wire 1/16" diameter. The metal dissolved was estimated by the potassium ferrocyanide colorimetric method.

1. Lake water containing 26·06 total solids; 0·0056 free NH_3; 0·0126 albumenoid NH_3; 1·756 Cl; in 24 hours dissolved 0·099 Cu.

2. Water containing 27·66 total solids; no free NH_3; 0·001 albumenoid NH_3; 1·22 Cl; dissolved in 24 hours 0·023 Cu.

3. Town water supply, 21·77 total solids; 0·55 SiO_2; 0·03 $Al_2O_3 \cdot P_2O_3$; 4·70 $CaSO_4$; 10·50 $CaCO_3$; 0·92 $MgCO_3$; 2·07 NaCl; 3·0 organic matter; after 94 hours contact dissolved 0·0825 Cu.

4. Free NH_3 water, and, therefore, free CO_2, after 115 hours contact contained 0·1925 Cu. By this time the water had absorbed both NH_3 and CO_2.

5. Distilled water in five months dissolved 0·055 Cu.

6. The following is the analysis of a sludge from a water tube boiler after being in use for some years. It is interesting as indicating a constant solvent action of the water on the copper and brass fittings :—H_2O, 13·12 per cent; SiO_2, 2·4 per cent; $Fe_2O_3 \cdot Al_2O_3$, 2·30 per cent; $CaCO_3$, 81·90 per cent; copper, 0·006 per cent.

Action on Lead.

These experiments were made with six different lengths of new lead piping, 2' long × ½" bore, cut from the same coil and closed at one end, each of which is distinguished by a number placed before the lead determination. These were treated by frequently filling and agitating with their respective waters during 24 hours, so as to corrode the

bright surfaces as much as possible. The two standard solutions used were prepared by dissolving 0·2 grm. of piping in acetic acid, and making up to 1000 c.c. with each water. Water A had a hardness of 3·5° before boiling and 3·2° after, and yielded a total residue of 8·5. Water B had a hardness of 18·6° before and 5° after boiling, and gave a total residue of 19·28. The former had a constant solvent action on lead while in practical use, whereas B had no action. Results are expressed in parts per 100,000.

	A.	B.
Pb dissolved in ½ hour ..	1. 0·99	—
,, ,, ½ ,, ..	2. 2·38	—
,, ,, 1 ,, ..	3. 3·37	4. 0·021
,, ,, 4 hours ..	1. 3·97	5. 0·049
,, ,, 21 ,, ..	2. 2·98	6. 0·099
,, ,, 120 ,, ..	3. 2·38	—

Here we see that the solvent power of A is 160, 81, and 30 times greater than B.

The pipes were washed, and filled with water charged with about 20 c.c. of CO_2 per pint, and in one hour A dissolved (1) 3·37 and B (4) 0·021, the same as the waters dissolved without gas.

Water A was almost saturated with CO_2, and dissolved in half an hour (2) 0·99, in one and a half hours (2) 5·96.

A saturated with CO_2, then agitated with precipitated $CaCO_3$, allowed to settle, and decanted clear unfiltered liquor into pipes, contained in one hour (3) 0·238; another experiment gave only trace.

Pint of A, mixed with 10 c.c. of saturated CaO solution, and allowed to settle for one hour, when the water gave faint alkaline reaction, thus showing slight excess of CaO, whereas the decanted clear liquid dissolved only a trace in one hour. Another experiment, but with the water heated after addition of CaO, dissolved 0·061.

When water A was thoroughly agitated with precipitated $CaCO_3$, and *filtered*, it did not dissolve any lead. Filtered through 3" of ¼" pieces of washed marble at the rate of half a pint per minute, dissolved no lead after seventy minutes contact.

AN EXAMINATION OF THE PRODUCTS OBTAINED BY THE DRY DISTILLATION OF BRAN WITH LIME.*

By W. F LAYCOCK, Ph D.

The Distillation.

TWENTY-TWO kilos. of wheat bran mixed with 44 kilos. of burnt lime were distilled in a large iron retort over a coal fire. The products of distillation passed over a large T-tube which was opened from time to time to draw off the distillate. The more volatile portion was led through a condenser having a worm 7 metres long placed in a tank filled with cold water.

Soon after applying heat to the retort, dense white fumes made their appearance in the receiver and continued to be evolved until the whole of the bran had been decomposed. The fumes had a strong characteristic smell. On ignition the escaping gases burnt with a pale luminous flame. The distillation proceeded quietly, and was finished in about seven hours. The residue in the retort was a grey mass containing particles of charcoal. The distillate consisted of a red-brown aqueous solution, with a black oil on its surface. The solution A was separated from the oil B.

Examination of A.

The aqueous solution, after filtering, measured 9·6 litres and weighed 9·7 kilos. It smelled of herring brine, and was strongly alkaline. On distilling a small quantity, crystals—which proved to be ammonium bicarbonate—were formed in the condenser. When a portion was acidified with hydrochloric acid, carbon dioxide was evolved, and a pine-splinter boiled in the liquid gave a brilliant pyrrol-reaction. The whole of the solution, together with 100 grms. of solid caustic potash, was placed in a large can and distilled with steam. When the distillate ceased to give the pyrrol-reaction the distillation was discontinued. On extracting the alkaline solution remaining in the still with ether, drying the extract with potassium carbonate and distilling, about 6 grms. of reddish-yellow oil (1) boiling at 190—310°* were obtained. The oil contained homologues of pyrrol, and gave on analysis 11 per cent nitrogen.

The Distillate from the Steam Distillation. — This weighed 1650 grms. It was a yellow aqueous solution, with a small quantity of oil on its surface. The oil was separated by filtration, dried, and distilled. About 3 grms. of oil (2) boiling at 130—240°, containing pyrrols and yielding 9 per cent nitrogen, distilled over.

The aqueous filtrate† was neutralised with hydrochloric acid, made slightly acid, and distilled with steam. The distillate, 1·5 litres, was distilled on the water-bath. About 77 grms. of a colourless oil passed over. The solution remaining in the distilling flask was saturated with potassium carbonate and extracted with ether. The extract yielded 15 grms. of an oil (3) boiling between 70—200°, and containing pyrrols and 11·5 per cent nitrogen.

The 77 grms. of colourless oil were distilled, 29 grms. (4) passing over between 62—90°. When the temperature reached 90° the liquid in the distilling flask suddenly became turbid and separated into an aqueous and an oily layer. The distillation was stopped at this point and the oily layer extracted with ether. About 2 grms. of colourless oil (5) boiling at 120—180° were obtained. This oil also contained pyrrols, and gave on analysis 12 per cent nitrogen.

The oils (1), (2), (3), *and* (5), *amounting to* 26 *grms.*, averaging about 11 per cent nitrogen and boiling between 70—310°, were mixed. Repeated attempts to isolate the pyrrols, and obtain fractions of constant boiling-point, failed owing to the presence of hydrocarbons and bases. The mixture was boiled for some time with hydrochloric acid to convert the pyrrols into pyrrol-red, and thus ascertain approximately their amount. On filtering the liquid 16 grms. of pyrrol-red were obtained.

The 29 *grms. of oil* (4) *boiling* 62—90° gave the following reactions:—The oil had a sweet smell. On shaking sodium bisulphite with it, no crystals separated, proving the absence of acetone. Ammoniacal silver nitrate, Fehling's solution, and a solution of magenta decolourised by sulphurous acid were not altered, consequently aldehyds were absent.

A portion treated with phenylhydrazine became warm and quite turbid, proving the presence of a ketone.

From 6 grms. of oil 2 grms. of a hydrazone were separated. On distilling this orange-red liquid hydrazone, it decomposed suddenly at about 90°. It behaved similarly under reduced pressure (420 m.m.) at about 80°.

* This investigation was carried out in the Laboratory of Prof. L. Knorr, at the University of Jena.

* *Colour Reactions with Pine-splinters.*—As the last drop passing over at 310° imparted a bright red colour to a pine-splinter on boiling with dilute hydrochloric acid, an indole is probably present. A pine-splinter dipped in an emulsion of water and the oil formerly termed "metacetone," becomes, on exposure to the vapour of hydrochloric acid, violet-blue. "Metacetone" consists chiefly of dimethyl furfurane mixed with a hydrocarbon (*Ber.*, xxii., 103). A pine-splinter simply boiled in water and exposed to hydrochloric acid vapour becomes emerald-green. It is probable that some pine-splinter reactions mentioned in chemical literature have been masked by the latter. Furfurane has been stated to give, under similar conditions, a green colour (*Ber.*, xx., Ref. 221).

† The filtrate gave the following reactions:—On adding potassium carbonate, ammonia and amines were evolved and an oil separated out. On extracting the latter with ether and evaporating, a small quantity of a very pungent smelling oil remained. On adding water and bringing a rod moistened with hydrochloric acid near it, white fumes were produced, showing the presence of organic bases. A solution of magenta decolourised by sulphurous acid was not affected, proving that aldehyds were absent.

Table I.

				Melting-point.	Calculated for—	Melting-point.
0·2017 grm.	Pt salt on ignition gave	0·0832 grm.	Pt = 41·25 per cent	228°	$(CH_3NH_2HCl)_2PtCl_4$. 41·19 per cent	
0·1131 „	„	0·0472 „	„ = 41·73 „	230°		
0·0969 „	„	0·0384 „	„ = 39·62 „	223°	$(C_2H_5NH_2HCl)_2PtCl_4$. 38·09 per cent	219°
0·0956 „	„	0·0366 „	„ = 38·28 „	223°		
0·2087 „	„	0·0775 „	„ = 37·13 „	228°	$(CH_3)_2N.HCl)_2PtCl_4$. 36·81 per cent	240—245°
0·1178 „	„	0·0436 „	„ = 37·01 „	237°		Decomposes.

Table II.—The Aqueous Solution A, 9·7 kilos.

Added 100 grms. KOH and distilled with steam.

- Alkaline residue extracted with ether, ethereal extract distilled, 6 grms., 250—310°, 11 per cent nitrogen, contains pyrrols. (1).
- Distillate—Aqueous solution, some oil which was filtered off.
  - Oil distilled, 3 grms., 130—240°, 9 per cent nitrogen, contains pyrrols. (2).
  - Aqueous filtrate, 1650 c.c., acidified with HCl, distilled with steam.
    - Distillate—Aqueous solution, some oil, distilled on water-bath.
      - Aqueous residue saturated with K_2CO_3, extracted with ether, ethereal extract distilled, 15 grms., 70—200°, 11·5 per cent nitrogen, contains pyrrols. (3).
      - Distillate—77 grms., fractionated.
        - Distillate—29 grms., 62—90°, contains ketones, alcohol. (4).
        - Residue boiling above 90° extracted with ether, ethereal extract, distilled, 3 grms., 120—180°, 12 per cent nitrogen, contains pyrrols. (5).
    - Acid residue boiled off pyrrols, filtered.
      - Filtrate evaporated to dryness, saline residue 350 grms. extracted with alcohol.
        - Alcoholic extract crystallised, 20 grms., hydrochloride of amine bases.
        - Residue—Ammonium chloride, about 300 grms.
      - Residue—Pyrrol-red, 3 grms.

On adding two or three drops of the oil to 1 c.c. of a freshly prepared half per cent solution of sodium nitroprusside, making up to 3 c.c. with water, and adding dilute caustic potash (1·14) until, just alkaline, a deep red colouration was produced. The colour turned violet-red on acidifying with acetic acid, proving methylpropyl ketone to be present (Béla von Bittó, *Ann. Chem. Pharm.*, 267, 372).

On warming the oil with glacial acetic acid, the smell of acetic ether was noticed. When iodine was dissolved in the oil, and sodium carbonate solntion added, and the mixture heated to 70° until decolourised, the characteristic smell of iodoform was observed. On cooling, the solution deposited yellow crystals of iodoform. These tests show the presence of ethyl alcohol.

Sodium acted violently on the oil, hydrogen being evolved, and a yellow amorphous mass remained. The liquid smelled of pyridine bases.

The oil contained 3·85 per cent nitrogen. The pine splinter reaction with hydrochloric acid was violet, demonstrating the presence of a furfuran homologue.

The Acid Residue from the Steam Distillation.—This was made strongly acid with hydrochloric acid, and boiled in a large basin for six hours, water being added occasionally. The pyrrols were thus volatilised or decomposed. After filtering off 3 grms. of pyrrol-red the solution was evaporated to dryness on the water-bath. About 350 grms. of a dark crystalline mass remained. This substance was purified by boiling with animal charcoal, filtering, and crystallising. The crystals of ammonium chloride obtained were extracted with alcohol, the alcoholic extract and the aqueous mother-liquor being eventually mixed and evaporated to dryness. The salts thus obtained were further purified by distillation with solid caustic potash, the vapours being absorbed in hydrochloric acid, and the resulting salts subjected to fractional crystallisation. Eventually three portions, almost free from ammonium chloride, were obtained, viz., 1 grm. of shining deliquescent plates, 2 grms. of long needles, and 17 grms. of uncrystallisable mother-liquor containing deliquescent needles.

Each fraction gave similar reactions. On boiling a portion with potash solution, a strong smell of herring-brine was produced, and the evolved gases burnt on ignition.

On boiling with chloroform and alcoholic potash, primary amines were detected by the characteristic smell of the carbamine evolved.

Portions of the different fractions were separately treated with platinum tetrachloride, and the resulting platinum salts dissolved in water and re-crystallised or precipitated with alcohol. A series of platinum compounds differing in crystalline form, melting-point, and constitution was the result, but owing to the small amount

of substance at disposal a more complete separation was not attempted. A number of analyses were made, and the results appear to agree fairly with well with known salts. (See Table I.).

Each of the above platinum salts decomposed on melting.

From these figures it is evident that methylamine, ethylamine, and trimethylamine formed part of the mixed salts.

(To be continued).

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THE IODOMETRIC DETERMINATION OF MOLYBDENUM.*

By F. A. GOOCH and JOHN T. NORTON, Jun.

(Concluded from p. 208).

During the first period of distillation the liquid assumed the clear green colour, which changed but slightly until the beginning of the third period, when the tint verged upon olive, and at the end of the operation the colour of the liquid was an olive brown which grew browner on cooling. The addition of considerable hydrochloric acid to the residual liquid restored the clear green colour, while water changed the olive brown to reddish yellow, the tint varying with the dilution. The results of these experiments are recorded in 1 to 5 of the accompanying table. In division A are given the weights of molybdenum trioxide corresponding to the amounts of iodine found in the three stages of distillation; in division B, the molybdenum trioxide corresponding to the iodine evolved from the beginning of the process to the end of each stage.

A.

	HCl (sp. g. 1·12) taken.	KI in retort.	MoO_3 taken as ammonium molybdate.	MoO_3 corresponding to iodine found. 1st Stage.—40 c.m.³ to 32 c.m.³. Green colour.	2nd Stage.—32 c.m.³ to 25 c.m.³.	3rd Stage.—25 c.m.³ to 10 c.m.³.
	C.m.³.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	40	0·5	0·2455	0·2399	0·0076	0·0004
2.	40	0·5	0·2455	0·2402	0·0053	0·0013
3.	40	0·5	0·2455	0·2414	0·0040	0·0004
4.	40	0·75	0·2455	0·2404	0·0061	0·0004
5.	40	0·75	0·2455	0·2431	0·0037	0·0004
6.	40	1·	0·2455	0·2404	0·0085	0·0019
7.	50	2·	0·2455	—	—	—

B.

	MoO_3 corresponding to iodine found during period of Friedheim and Euler. (1st stage).	Error.	MoO_3 corresponding to iodine found in concentrating from 40 c.m.³ to 25 c.m.³.	Error.	MoO_3 corresponding to iodine found in concentrating from 40 c.m.³ to 10 c.m.³.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·2399	0·0056—	0·2475	0·0020+	0·2479	0·0024+
2.	0·2402	0·0053—	0·2455	0·0000	0·2468	0·0013+
3.	0·2414	0·0041—	0·2454	0·0001—	0·2458	0·0003+
4.	0·2404	0·0051—	0·2465	0·0010+	0·2469	0·0014+
5.	0·2431	0·0024—	0·2468	0·0013+	0·2472	0·0017+
6.	0·2404	0·0051—	0·2489	0·0034+	0·2508	0·0053+
7.	—	—	—	—	0·2495	0·0040+
					0·2529*	0·0074+

* On repeating distillation with a fresh charge of acid.

The mean error of the indications taken during the period of distillation advocated by Friedheim and Euler is 0·0045 grm.—;† that of the period of concentration from 40 c.m.³ to 25 c.m.³ is 0·0008 grm.+; and that of the full period of distillation is 0·0014+. It is plain beyond a peradventure that in the process as conducted by Friedheim and Euler, excepting the protection against atmospheric action, the theoretical reduction of the molybdic acid does not take place. The best results are obtained when the distillation is prolonged until the original volume of 40 c.m.³ has been diminished to 25 c.m.³. Concentration beyond the limit of 25 c.m.³ tends to develop a tendency toward over-reduction, especially when the amount of potassium iodide is increased beyond about 0·5 grm. in excess of that theoretically required. This is shown in Experiments 6 and 7, conducted otherwise similarly to those described above, in which the amount of potassium iodide was increased to 1 grm. and 2 grms. The error after distilling from 40 c.m.³ to 10 c.m.³, the lowest limit of the preceding experiments, was 0·0053 grm.+ and 0·0040 grm.+, and the latter error was increased to 0·0074 grm.+ on repeating the distillation with a fresh portion (30 c.m.³) of the acid. It is interesting to note incidentally that in the experiment in which the largest amount of iodide (2 grms.) was used the solution did not take the green colour at any stage of the distillation, probably because the large excess of iodide held the free iodine and so masked the colour until the degree of concentration was reached at which the olive-brown colour displaces the green.

The possibility of the interaction of atmospheric oxygen and gaseous hydriodic in the analytical process, even to the extent of producing errors of from 1 to 3 per cent reckoned as molybdenum trioxide, was recognised by Friedheim and Euler; and it was to obviate this difficulty that the recommendation was made by them to warm very gradually the distillation flask filled two-thirds with the mixture of iodide, molybdate, and acid, and to raise the liquid to actual boiling only when the space above the liquid in the retort and in the connecting tube is filled as completely as possible with iodine vapour, while the liquid in the receiver begins to rise in the tube.

The action of atmospheric oxygen upon the solution of hydriodic acid must, however, be also taken into account. It is a familiar fact that when a considerable excess of strong hydrochloric acid is allowed to act in contact with air upon potassium iodide (free from iodate) dissolved in a little water, the mixture is coloured by free iodine. The amount of iodine liberated by atmospheric action is insignificant when the acid is very dilute, but is considerable when the acid is strong, and increases with time and rise in temperature, as shown in the experiments recorded in the accompanying table.

KI taken.	Volume.	Percentage of HCl in aqueous acid.	Time in minutes.	Temperature, Centigrade.	$GMoO_3$ equivalent to iodine found.	Remarks.
Grm	C.m.³.				Grm.	
	166	2	1	23°	none	
1	66	2	10	23°	0·0001	
1	66	24*	10	23°	0·0017	Diluted to 500 c.m.³ before titrating with $Na_2S_2O_3$.
1	66	24*	4	From 23° to the boiling point.	0·0067	
1	66	24*	10		0·0121	

* This corresponds nearly to sp. gr. 1·12.

Even the precaution to conduct the operation in an atmosphere of carbon dioxide does not eliminate all chance of error of this sort unless the liquid of the mixture —the hydrochloric acid—is free from air. The experi-

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vi., 1898.

† Even this figure does not disclose the full error, which is partly counterbalanced, as will appear later, by the effect of oxygen dissolved in the acid used in the process.

ments of the following statement, which were conducted in the apparatus and manner previously described, show this point clearly. Thus, 40 c.m.³ of unboiled acid, sp. gr. 1·12, introduced enough air into the apparatus to cause an error of 0·0013 grm., reckoned in terms of molybdenum trioxide, while the iodine set free by the action of the residual acid of this experiment upon another grm. of potassium iodide introduced without admission of air corresponded to only 0·0002 grm. in terms of molybdenum trioxide. The use of acid of sp. gr. 1·1, freshly boiled in the air, obviously reduces the error due to the unboiled acid, but even in this case the effect of included oxygen was not wholly obviated.

KI taken.	Volume.	Percentage of HCl in aqueous acid.	Concentration by boiling.	MoO_3 equivalent to iodine found.	Remarks.
Grm.	C.m.³.		C.m.³.	Grm.	
1	40	24	40—30	0·0013	Iodine determined in distillate.
			30—20	0·0002	1 grm. of KI added to retort at the beginning of the 2nd stage.
1	40	20	40—25	0·0005	The acid taken, sp. gr. 1·1, was freshly boiled and introduced at once upon KI in retort in CO_2.

It is obvious that the procedure recommended by Friedheim and Euler can by no possibility eliminate the effect of atmospheric action upon the mixture of acid and iodide. The extent of such action must depend upon such conditions as the size of the apparatus, the time of exposure, the body of air above and dissolved in the liquid, and the rate of displacement of the air. How great the error due to atmospheric action actually was in the process as conducted by Friedheim and Euler we, of course, have no means of knowing. It is to be hoped, however, that it was sufficiently great to counterbalance that other inevitable error (of about 5 m.grms.) which exists by reason of the incompleteness with which molybdic acid is reduced under the conditions which these investigators prescribe; for the value of Euler's work upon the vanadiomolybdates rests upon the chance that these two very considerable and indisputable tendencies to error may have neutralised one another.

It has been shown clearly that our former criticism of the procedure of Friedheim and Euler is justified in every particular. We have no change to make in the recommendation made therein as to necessary modifications.

If the conditions seem difficult, there is an alternative in the method proposed in the former article (*Am. Journ. Sci.*, IV., ii., 156), according to which the molybdate is reduced by the acid and iodide in an Erlenmeyer beaker (trapped loosely by means of a short bulbed tube hung in the neck), and the molybdenum pentoxide, freed from iodine by boiling, is reoxidised by standard iodine in alkaline solution.

ON THE DETECTION OF SULPHIDES, SULPHATES, SULPHITES, AND THIOSULPHATES, IN THE PRESENCE OF EACH OTHER.*

By PHILIP E. BROWNING and ERNEST HOWE.

Some three years ago R. Greig Smith (Chemical News, vol. lxxii., 39) published a method for the detection of sulphates, sulphites, and thiosulphates in the presence of each other, which promised much toward the solution of this most difficult problem. The method may best be described in the author's own language:—To a solution of the salts of the above-mentioned acids "barium chloride is added in excess, together with a good quantity of ammonium chloride, which, like many salts of ammonium, potassium, and calcium, acts as a flocculent or coagulant, and facilitates the filtration of the barium sulphate. Hydrochloric acid is next added, drop by drop, until it is evident that there is no further solution of barium sulphite and thiosulphate, and that only the sulphate remains undissolved; the solution is then filtered through a moistened double filter-paper, which should be free from 'pin holes.' The filtrate will probably be clear, but if not it should be returned to the filter for a second filtration. When too much thiosulphuric acid is present, the clear filtrate will visibly become clouded, or from being whitish will become more opaque; if this occurs the solution should be thrown out, and a fresh portion made more dilute. A solution of iodine is added to half of the filtrate until the colour is of a permanent yellow tinge; a white precipitate indicates the presence of a sulphite which has been oxidised by the iodine to sulphate. In the absence of a decided precipitate traces of sulphite may easily be detected by comparing the treated and untreated halves of the filtrate—a procedure which very often saves a good deal of time, as it is unnecessary to wait until a clear filtrate is obtained. The two halves are mixed, and if the yellow colour disappears more iodine is added, the solution filtered, and the filtrate divided into two halves as before. With a slight turbidity filtration may be omitted. Bromine water is added to one of the halves when any thiosulphate in the original solution shows itself as a white precipitate of barium sulphate, readily seen on comparing the two test-tubes. The thiosulphate is by iodine converted to tetrathionate, which is oxidised by bromine water to sulphate." Three objections to this method as described will readily occur to the reader: first, the readiness with which the thiosulphate is decomposed by free hydrochloric acid; second, the comparatively large amount of acid necessary to effect the complete solution of the barium sulphite and thiosulphate when precipitated with the sulphate as compared with the amount required to prevent the precipitation; third, the lack of delicacy necessitated by a comparison of portions of a coloured solution in looking for small precipitates. The work to be described was undertaken to overcome these difficulties and to test the accuracy of a modified method. Solutions of potassium sulphite and sodium thiosulphate were made approximately decinormal and standardised in the usual manner against an iodine solution of known value. It was found that by making a solution containing sulphates, sulphites, and thiosulphates very faintly acid, the sulphates and thiosulphates were held completely in solution when the barium sulphate was precipitated. The extreme sensitiveness of a thiosulphate to the decomposing action of free hydrochloric acid suggested the possible substitution of acetic acid to hold the sulphites and thiosulphates in solution. This being a weaker acid, we hoped to avoid the decomposition of the thiosulphate into sulphur and sulphurous acid, or at least to delay the decomposing action. The results of these experiments appear in Table I.

From these results it would seem that the decomposition of a thiosulphate is more rapid in presence of hydrochloric acid than in presence of a much larger amount of acetic acid.

Our next experiments were directed toward a determination of the effect of adding stannous chloride to bleach the colour of the free iodine and bromine used in the oxidation and of acidifying with acetic acid, before treating with barium chloride. That is to say, the process as we used it consisted in acidifying the solution to be tested with acetic acid, adding barium chloride, filtering to remove precipitated sulphate (always present in the

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. vi., Oct., 1898.

TABLE I.

	Volume c.m.s of water.	Hydrochloric acid (1 : 4). Drops.	Acetic acid. Drops.	$Na_2S_2O_3$ taken. Grm.
1.	10	2	—	0·01 (*a*)
2.	10	2	—	0·1 (*b*)
3.	100	3	—	0·1 (*c*)
4.	10	—	8	0·01 (*d*)
5.	10	—	8	0·1 (*e*)
6.	100	—	10	0·1 (*f*)
7.	100	—	10	0·25 (*g*)
8.	100	—	10	0·5 (*h*)
9.	100	—	10	1·0 (*i*)

Result.

(*a*) No sulphur in 20 minutes.
(*b*) Sulphur in 45 seconds.
(*c*) Sulphur in 15 minutes.
(*d*) No sulphur in 20 minutes.
(*e*) Sulphur in 90 seconds.
(*f*) No sulphur in 20 minutes.
(*g*) Sulphur in 15 minutes,
(*h*) Sulphur in 60 seconds.
(*i*) Sulphur in 30 seconds.

TABLE II.

	K_2SO_3 taken. Grm.	Volume of water. C.m.s.	$BaSO_4$ precipitated after oxidation with iodine.
1.	0·1	10	Very abundant (*a*)
2.	0·01	10	Abundant (*b*)
3.	0·001	10	Distinct (*c*)
4.	0·0005	10	Fair (*d*)
5.	0·0001	10	Faint (*e*)

Remarks.

(*a*) Plainly visible before adding $SnCl_2$.
(*b*) Plainly visible before adding $SnCl_2$.
(*c*) More distinct after adding $SnCl_2$.
(*d*) Hardly visible before adding $SnCl_2$.
(*e*) Invisible before adding $SnCl_2$.

TABLE III.

	$Na_2S_2O_3$ taken. Grm.	Volume of water. C.m.s	$BaSO_4$ precipitated by action of iodine.	$BaSO_4$ precipitated by action of bromine.
			A.	
1.	0·1	10	Distinct	Abundant (*a*)
2.	0·01	10	Faint	Abundant (*b*)
3.	0·001	10	None	Distinct (*c*)
4.	0·0005	10	None	Faint (*d*)
5.	0·0001	10	None	Very faint (*e*)

Remarks.

(*a*) Sulphur separated in 30 seconds.
(*b*) No sulphur in 90 seconds.
(*c*) No sulphur in several minutes.
(*d*) No sulphur; $SnCl_2$ necessary.
(*e*) No sulphur; $SnCl_2$ necessary.

			B.	
1.	0·1	10	Faint	Abundant (*a*)
2.	0·01	10	None	Abundant (*b*)
3.	0·001	10	None	Distinct (*c*)
4.	0·0005	10	None	Faint (*d*)
5.	0·0001	10	None	Very faint (*e*)

Remarks.

(*a*) No sulphur separated in 1 minute.
(*b*) No sulphur separated in several minutes.
(*c*) No sulphur.
(*d*) No sulphur; $SnCl_2$ necessary.
(*e*) No sulphur; $SnCl_2$ necessary.

sulphite), adding iodine to the filtrate until the colour was permanent, bleaching with stannous chloride, filtering off the sulphate which represents the sulphite originally present, adding bromine in excess to the filtrate, and again bleaching with stannous chloride to increase the visibility of the sulphate which now represents the thiosulphate originally present. The details of experiments in which the sulphite was taken alone and oxidised with iodine are given in Table II.

A corresponding series of experiments was made in which hydrochloric acid was substituted for acetic acid, and essentially the same results were obtained.

A similar series of experiments was made to test the effect of treating the thiosulphate in an acidified solution, first with iodine and then after filtration (if a precipitate had formed) with bromine. In the experiments of division A hydrochloric acid (a few drops) was added before treating with barium chloride, and in those of division B acetic acid was used similarly. Stannous chloride was employed to bleach the excess of iodine and bromine. (See Table III.).

From these experiments the advantage of the use of acetic acid becomes apparent, as does also the use of stannous chloride in increasing the delicacy of this indication, so that a small fraction of a milligramme may easily be detected.

If relatively large amounts of thiosulphate are present with small amounts of sulphite, we have sometimes found it advantageous to manipulate so that even the slow decomposition of the thiosulphate by acetic acid may be avoided by first attempting precipitation with barium chloride in a dilute ammoniacal solution. By this method the barium sulphate and sulphite are separated from the thiosulphate and identified—the sulphate by its insolubility in dilute hydrochloric acid, and the sulphite by the action of iodine upon the acid filtrate from the barium sulphate. After filtering, the thiosulphate may be detected in the filtrate by the use of iodine and bromine as described above. Table IV. gives some results by this treatment.

TABLE IV.

	$Na_2S_2O_3$ taken. Grm.	$BaSO_4$ precipitated by iodine.	$BaSO_4$ precipitated by bromine.	Remarks.
1.	0·1	None	Abundant	
2.	0·01	None	Good	
3.	0·001	None	Fair	$SnCl_2$ necessary.
4.	0·0005	None	Faint	$SnCl_2$ necessary.
5.	0·0001	None	None	

As will be seen, the test for the thiosulphite by this method of treatment is not so delicate, probably on account of mechanical holding of the barium thiosulphate by the precipitated sulphate and sulphite.

Having determined the limits of accuracy of the method as applied to the sulphite and thiosulphate taken separately, our next experiments were directed toward an investigation of the working of the method when these two acids are found together in solution. Sulphates, almost invariably present with sulphites, are of course quite easily separated by filtration and treating with the barium salt in acid solution. Sulphides if present in the solution would seriously interfere with the working of this method if not removed, being readily oxidised by the iodine or bromine to sulphite, sulphate, or, should sulphur also separate, to thiosulphate. We found in course of our work that in attempting to neutralise a mixture of freshly prepared alkaline sulphide together with a sulphite, we often obtained a precipitate of sulphur. After the removal of the sulphide and sulphate, we were surprised to find on treating with iodine scarcely a trace of sulphite. On treating with bromine, however, an abundant indication of thiosulphate was obtained. It is well known, of course, that thiosulphate may be found by boiling a sulphite with sulphur, but that this reaction should take place so readily and completely seemed to us rather unusual.

For the removal of a sulphide before proceeding with the tests for sulphite and thiosulphate, Grieg Smith recommends the passing of carbon dioxide through the solution until the escaping gas gives no indication of hydrogen sulphide, but Bloxam (CHEM. NEWS, lxxii., 63)

calls attention to the tedious and wholly unsatisfactory character of this method of removal, and recommends a mixture of zinc chloride, cadmium chloride, ammonium chloride, and ammonia. We have found that the addition of zinc acetate to a faintly alkaline solution accomplishes the same purpose in an entirely satisfactory manner. The sulphide used in our work was freshly made by passing hydrogen sulphide through a dilute solution of sodium hydroxide. When portions of this solution, still alkaline, were treated with zinc acetate in excess, and the zinc hydroxide and sulphide removed by filtration, the filtrate gave no test for either sulphite or thiosulphate by the application of iodine and bromine as described, and the vapour evolved on boiling caused no darkening of lead paper. The following table shows the results of a few experiments in which tests were made for the sulphite and thiosulphate, after removing a considerable amount of the sulphide in the manner described, and of the sulphate by acidifying and adding barium chloride.

TABLE V.

K_2SO_3 taken. Grm.	$Na_2S_2O_3$ taken. Grm.	$BaSO_4$ precipitated after oxidation with iodine.	$BaSO_4$ precipitated after oxidation with bromine.
0·1	0·01	Abundant	Good.
0·1	0·001	Abundant	Distinct.
0·01	0·1	Good	Abundant.
0·001	0·1	Faint	Abundant.
0·001	0·001	Fair	Fair.

The method as we have modified it may be summarised as follows:—To about 0·1 grm. of the substance to be analysed dissolved in 10 c.m.³ of water or more, add sodium, potassium, or ammonium hydroxide to distinct but faintly alkaline reaction. The solution should be neutral or alkaline rather than even faintly acid, owing to the readiness with which sulphur separates. To the alkaline solution add zinc acetate in distinct excess, and filter. The precipitate may be tested for hydrogen sulphide, on acidifying, in the usual manner. To the filtrate add acetic acid, a few drops in excess of the amount necessary to neutralise, and barium chloride, and filter through a double filter. To the filtrate add iodine until the solution takes on a permanent yellow tinge, and then bleach with stannous chloride,—best after adding a few drops of hydrochloric acid to prevent the possible precipitation of a basic salt of tin. A precipitate at this point indicates the sulphite. Filter, add bromine water in faint excess to the filtrate, bleaching again with stannous chloride. A precipitate on adding bromine indicates a thiosulphate originally present.

THE

ACTION OF LIGHT UPON DYED COLOURS.*

(Concluded from p. 206).

CLASS III.—MODERATELY FAST COLOURS. (WOOL).

Induline Colours.

Wool Book XIV.

Acid Colours.—

*9. Nigrisine. Sodium salt of an induline-sulphonic acid. S. and J. III. 475.
*10. Brilliant Black EB. Constitution not published.

Basic Colours.—

2*a*. Nigrisine J. Condensation product of *p*-nitroso-dimethyl aniline.
3*a*. Nigrisine. Similar to Nigrisine J. S. and J. III. 502.

Azo Colours.

Acid Colours.—

*5. Naphthol Black 4R. Constitution not published.
8. Jet Black R. From amido-benzene-disulphonic-acid-azo-α-naphthylamine and phenyl-α-naphthylamine. S. and J. III. 150.
11. Naphthylamine Black. From α-naphthylamine disulphonic-acid-azo-α-naphthylamine and α-naphthylamine. S. and J. III. 153.
*41. Acid Black B. Constitution not published.
16. Acid Black 2B. Constitution not published.
*17. Naphthol Black 6B. From α-naphthylamine-disulphonic acid-azo-α-naphthylamine and β-naphthol-disulphonic acid R. S. and J. III. 154.
*18. Naphthol Black 3B. Constitution not published.
*20. Victoria Black B. From sulphanilic acid-azo-α-naphthylamine and β-naphthol-sulphonic acid S. S. and J. III. 149.
*22. Naphthol Black B. From β-naphthylamine-γ-disulphonic acid-azo-α naphthylamine and β-naphthol-disulphonic acid R. S. and J. III. 157.
25. New Victoria Black Blue. Constitution not published.
28. Naphthylamine Black 6B. Constitution not published.
*29. Victoria Black Blue. Constitution not published.
30. Naphthylamine Black 4B. Constitution not published.
31. New Victoria Black B. Constitution not published.
*32. Victoria Black G. Constitution not published.
*33. Victoria Black 5G. Constitution not published.
34. New Victoria Black 5G. Constitution not published.

Wool Book XIV.

Basic Colours.—

*3. Diazine Black. From safranine and phenol.

Direct Cotton Colours.—

3. Benzo Black Blue G. From benzidine-disulphonic acid, with α-naphthylamine-azo-α-naphthol-sulphonic acid NW and α-naphthol-sulphonic acid NW. S. and J. III. 266.
4. Benzo Black Blue R. From tolidine, with α-naphthylamine-azo-α-naphthol-sulphonic acid NW and α-naphthol-sulphonic acid NW. S. and J.III. 266.
5. Benzo Black. Constitution not published.
6. Benzo Black S extra. Constitution not published.
7. Diamond Jet Black OO. Constitution not published.
8. Chicago Grey. Constitution not published.
9. Diamine Jet Black SS. Constitution not published.
15. Diamine Black HW. Constitution not published.
17. Benzo Black Blue 5G. From benzidine-disulphonic acid, with α-naphthylamine-azo-dioxynaphthalene-sulphonic acid S and dioxynaphthalene-sulphonic acid S. S. and J. III. 267.

Direct Cotton Colours Developed.—

6. Diazo Brilliant Black B. From tolidine and α-naphthylamine-sulphonic acid L. Developed with β-naphthol.
7. Diazo Brilliant Black R. Constitution not published. Developed with β-naphthol.

Mordant Colour.—

1. Chrome Black (Cr). Constitution not published.
3. Diamond Black (Cr). From amido-salicylic-acid-azo-α-naphthylamine and α-naphthol-sulphonic acid NW. S. and J. III. 159.
4. Diamond Black NG (Cr). Constitution not published.
5. Diamond Black GA (Cr). Constitution not published.

* Report of Committee, consisting of Dr. T. E. Thorpe (Chairman), Professor J. J. Hummel (Secretary), Dr. W. H. Perkin, Professor W. J. Russell, Captain Abney, Professor W. Stroud, and Professor R. Meldola. (Drawn up by the Secretary). Read before the British Association (Section B), Bristol Meeting, 1898.

Natural Colouring Matters.

Mordant Colours.—

Logwood (Cr) (Fe*). Hæmatoxylon campecianum (wood).

Cochineal (Fe*). Coccus cacti (insect).

NOTES.—The colours dyed with the two Nigrisines are medium shades of grey; they do not alter materially in hue during the fading process, and at the end of the third period of exposure they still appear as pale greys. The following colours alter very little in hue while fading, and fade so gradually that they might fairly well be thought worthy of being classed as "Fast Colours":—Nigrisine, Brilliant Black EB, Acid Black B, Naphthol Blacks 3B and 6B, Victoria Blacks B, G, and 5G, Victoria Black Blue. Diazine Black acquires a somewhat yellowish cast at the end of the first period of exposure, and then fades so slowly that even at the end of a year a full grey shade remains.

Several of the artificial black colours in this class are quite as fast to light as the black obtained with logwood on chromium mordant; some indeed seem to be more permanent, and they do not acquire the characteristic olive tint of the faded logwood and chromium black. With iron mordant logwood gives a somewhat faster black than that obtained with chromium; the same appears to be the case with Chrome Black and the various marks of Diamond Black.

CLASS IV.—FAST COLOURS. (WOOL).

Azo Colours.

Wool Book XIV.

Mordant Colours.—

5. Chrome Black (Fe). Constitution not published.
6. Diamond Black (Fe). From amido-salicylic acid-azo-α-naphthylamine and α-naphthol-sulphonic acid NW. S. and J. III. 159.
7. Diamond Black NG (Fe). Constitution not published.
8. Diamond Black GA (Fe). Constitution not published.

Oxyketone Colours.

Mordant Colours.—

*Alizarin Black SW (Cr) (Fe). Sodium bisulphite compound of dioxy-naphthoquinone. S. and J. III. 385.

*Alizarin Bordeaux G (Fe). Constitution not published.

*Alizarin Bordeaux B (Fe). Tetra-oxy-anthraquinone (1.2.5.8). Quinalizarin. S. and J. III. 403.

CLASS V.—VERY FAST COLOURS. (WOOL).

Oxyketone Colours.

Wool Book XIV.

Mordant Colours.—

Alizarin Bordeaux GG (Fe). Constitution not published.

Silk Patterns.

Most of the foregoing colours were also dyed on silk, and the patterns were exposed to light along with the woollen patterns. The relative fastness of the various colours is generally the same as on wool, and a special classification for silk seems unnecessary.

DISTRIBUTION AND QUANTITATIVE OCCURRENCE OF VANADIUM AND MOLYBDENUM IN ROCKS OF THE UNITED STATES.*

By W. F. HILLEBRAND.

ASIDE from its well known mineral combinations, vanadium has long been known to occur in magnetites and other iron ores. Hayes in 1875 reported its occurrence in a great variety of rocks and ores. Quoting from "Thorpe's Dictionary of Chemistry," "it is said to be diffused with titanium through all primitive granite rocks (Dieulafait) and has been found by Deville in bauxite, rutile, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands . . . ." It is further reported to comprise as V_2O_5 0·02 to 0·07 per cent of many French clays, 0·02 to 0·03 per cent of some basalts, 0·24 per cent of a coal of unknown origin and 0·45 per cent of one from Peru, amounting to 38·5 per cent ond 38 per cent of the ash and noted respectively by Mourlot and Torrico y Meca. Doubtless many other instances of its occurrence have been noted.

In Table I. is shown its quantitative occurrence and distribution in a large number and variety of igneous rocks of the United States, arranged according to their silica contents; and in Table II. the same data are given for a few of the component minerals separated from some of those rocks, while Table III. shows its presence in metamorphosed and secondary rocks by a few examples of roofing slates and schists, and especially by two composite samples representing 253 sandstones and 498 building limestones. These last two afford positive proof of its general distribution through rocks of those classes. Incidentally some information has been acquired as to molybdenum. Owing to lack of entire certainty as to its condition of oxidation, the vanadium is tabulated in terms of both V_2O_5 and V_2O_3, a point which will be reverted to later on. With very few exceptions, the amount of each sample taken for analysis was 5 grms. The reagents used were carefully tested and found free from vanadium and molybdenum. Except Nos. 38, 39, 47, 52, and 53, by Dr. H. N. Stokes, all determinations are by myself.

Of the igneous rocks specimens were so selected as to represent not only many widely separated localities, but also numerous varieties from the least siliceous up to those high in silica, in order to ascertain whether a preconceived opinion that the vanadium accompanied chiefly the less siliceous rocks was well founded or not. The choice was, however, confined largely to those rocks analysed in this laboratory within the past three or four years of which a supply of powder remained after the original analyses had been completed, and hence the list is perhaps not fully representative. Nevertheless it permits of drawing certain conclusions, the chief of which is that the vanadium predominates in the less siliceous igneous rocks and is absent—or nearly so—in those high in silica. The inference, based on the existence of the mineral roscoelite, classed as a vanadium-mica, at once suggests itself, that the ultimate source of the vanadium may be one or more of the heavier silicates—such as the biotites, pyroxenes, and amphiboles, and a few tests on all the available mineral separation products lend strong support to this view. For instance, the amphibole gabbros 7 and 11 show 0·038 per cent and 0·02 per cent V_2O_3, while the anphiboles 7*a* and 11*a* separated from them give 0·062 per cent and 0·037 per cent; the pyroxenic gneiss 23 shows 0·083 per cent against 0·127 from its contained biotite 23*a*; the diorite 29 with 0·031 per cent contains an amphibole 29*a* with 0·066 per cent; from 0·011 per cent in the quartz-mica diorite 45 and 0·012 per cent in the quartz monzonite 46 the percentages rise to 0·048 and 0·066 in their separated biotites 45*a* and 46*a*. The pyroxene 21*a* shows, however, practically the same amount as its mother rock, the syenitic lamprophyre 21.

In most of these cases, notably the last one, the vanadium in the separated mineral is not sufficiently in excess of that in the rock from which it was taken to account for all of that found in the latter. Hence, if the determinations are correct, it must also be a constituent of some other mineral than the one analysed. In roscoelite the trivalent condition of vanadium corresponding to the oxide V_2O_3 is now recognised as probable, although Roscoe's analysis reports V_2O_5, and Genth's an oxide intermediate

* Read before the Geological Society of Washington, D.C., May 25, 1898. From the *American Journal of Science*, vol. vi., p. 209,

TABLE I.—*Igneous Rocks.*

No.	Name and locality of occurrence.	SiO_2. Per cent.	V_2O_5 = V_2O_3. Per cent.	V_2O_3. Per cent.	Mo. Per cent.
1.	Melilite-nepheline basalt, Uvalde Co., Texas	38	0·054	0·045	
2.	Nephelinite, Uvalde Co., Texas	40	0·042	0·035	
3.	Saxonite, Douglas Co., Oregon	41·5	None	None	
4.	Diorite, Cecil Co., Maryland	44	0·062	0·052	
5.	Gabbro, Adirondack region, New York	45	0·02	0·017	
6.	Plagioclase basalt, Uvalde Co., Texas	45	0·048	0·04	
7.	Amphibole gabbro, Alpine Co., California	46	0·046	0·038	None
8.	Plagioclase gneiss, Amador Co., California	46·5	0·033	0·027	
9.	Diorite, Mitchell Co., North Carolina	47	0·05	0·042	
10.	Porphyry, La Plata Co., Colorado	47	0·06*	0·05*	
11.	Amphibole gabbro, Tuolumne Co., California	47	0·024	0·02	None
12.	Orthoclase-bearing basalt, Uvalde Co., Texas	48?	0·048	0·04	
13.	Orthoclase-bearing basalt, Uvalde Co., Texas	48	0·02	0·017	
14.	Norite, Cecil Co., Maryland	48	0·023	0·019	
15.	Gabbro, Union Co., Tennessee	48	0·038	0·032	
16.	Gabbro, Douglas Island, Alaska	48	0·055	0·046	None
17.	Nepheline basanite, Colfax Co., North Mexico	48·5	0·044	0·037	
18.	Olivine basalt, Kruzoff Island, Alaska	49·5	0·054	0·045	None
19.	Diabase, Mt. Ascutney, Vermont	49·5	0·034	0·028	
20.	Phonolite, Cripple Creek, Colorado	50	0·033	0·027	
21.	Syenite lamprophyre, Prowers Co., Colorado	50·5	0·04	0·033	
22.	Augite-andesite porphyry, Electric Peak, Wyoming	50·5	0·045	0·038	
23.	Pyroxenic gneiss, Calaveras Co., California	51·5	0·10	0·083	None
24.	Labradorite porphyrite, Michigamme iron district, Michigan	52·5	0·048	0·04	
25.	Pyroxenite, Cecil Co., Maryland	53	0·04	0·034	None
26.	Orendite, Sweetwater Co., Wyoming	54	0·022	0·018	
27.	Andesite, El Paso Co., Colorado	54?	0·018	0·015	Trace?
28.	Nepheline syenite, El Paso Co., Colorado	54·5	0·022	0·018	Trace?
29.	Diorite, Butte and Plumas Cos., California	54·5	0·037	0·031	None
30.	Quartz diorite, Cecil Co., Maryland	55	0·043	0·036	None
31.	Diorite, La Plata Co., Colorado	55·5	0·038	0·032	
32.	Camptonite? San Miguel Co., Colorado	55·5	Lost, but considerable.		
33.	Phonolite, Colfax Co., North Mexico	56	Trace	Trace	
34.	Augite-bronzite andesite, Unga Island, Alaska	56·5	0·046	0·038	None
35.	Andesite, El Paso Co., Colorado	57?	0·025	0·021	Trace?
36.	Spilosite, Michigamme iron district, Michigan	58	0·03	0·025	None
37.	Hornblende granite, Cecil Co., Maryland	58·5	0·022	0·018	None
38.	Latite, Tintic district, Utah	60	0·007	0·006	None
39.	Monzonite, Tintic district, Utah	60	0·024	0·02	Trace
40.	Diorite porphyry, La Plata Mts., Colorado	60·5	0·02	0·017	
41.	Trachyte-andesite tuff, Tuolumne Co., California	62·5	0·017	0·014	
42.	Diorite, Douglas Island, Alaska	63	0·012*	0·01*	None
43.	Rhyolite, San Miguel Co., Colorado	64·5	0·004	0·003	Trace
44.	Syenite, Mt. Ascutney, Vermont	65·5	Trace?	Trace?	
45.	Quartz-mica diorite, Tuolumne Co., California	65·5	0·013	0·011	Trace
46.	Quartz monzonite, Calaveras Co., California	67	0·014	0·012	None
47.	Rhyolite, Tintic district, Utah	69	0·009	0·008	Trace
48.	Quartz diorite, Amador Co., California	69·5	0·005	0·004	Trace
49.	Trachyte, Highland Co., Virginia	69·5	Trace?	Trace?	
50.	Biotite granite, Amador Co., California	70·5	Trace	Trace	Trace
51.	Rhyolite, Crater Lake, Oregon	71	0·004	0·003	Faint trace
52.	Monzonite (altered), Tintic district, Utah	71	0·021	0·017	None
53.	Rhyolite quartz-porphyry, Tintic district, Utah	71·5	0·016	0·013	None
54.	Rock between rhyolite and dacite, Sutter Co., California	71·5	Trace	Trace	
55.	Syenite porphyry, Mt. Ascutney, Vermont	73	None	None	
56.	Granite porphyry, Mt. Ascutney, Vermont	73·5	None	None	
57.	Granite, Union Co., Tennessee	76·5	None	None	

* Approximate.

TABLE II.—*Component Minerals from certain of the above Igneous Rocks.*

No.	Name and source.	SiO_2. Per cent.	V_2O_5 = V_2O_3. Per cent.	V_2O_3. Per cent.	Mo. Per cent.
7*a*.	Amphibole from 7	?	0·075	0·062	None
11*a*.	Amphibole from 11	46	0·044	0·037	None
21*a*.	Pyroxene from 21	51·5	0·043	0·036	
23*a*.	Biotite from 23	36·5	0·153	0·127	None
29*a*.	Amphibole from 29	50	0·08	0·066	
45*a*.	Biotite from 45	?	0·057	0·048	None
46*a*.	Biotite from 46	35·5	0·08	0·066	

TABLE III.—*Miscellaneous.*

No.	Name and locality of occurrence.	SiO_2. Per cent.	$V_2O_5 = V_2O_3$. Per cent.	V_2O_3. Per cent.	Mo. Per cent.
58.	Epidotic schist, Mitchell Co., North Carolina	48	0·057	0·047	
59.	Quartz schist, Madera Co., California	79	Trace	Trace	
60.	Serpentine, Connecticut Valley, Massachusetts	38·5	None	None	
61.	Sea green roofing-slate, West Pawlet, Vermont	68	0·017	0·014	
62.	Two red roofing-slates (equal parts), Washington Co., New York	67 56	0·008	0·007	
63.	253 sandstones	78·5	0·003	0·003	
64.	498 building limestones	14	0·004	0·004	

between V_2O_3 and V_2O_5. This assumption seems to be necessary if the mineral is to be regarded as a mica, and it is then doubtless the equivalent of trivalent iron or aluminum. It would then be natural to look for it in the aluminous or ferric silicates of igneous rocks, certain biotites, pyroxenes, and hornblendes, and its absence in such minerals as serpentine and chrysolite, as shown by analyses 3 and 60, appears natural enough.

Few and inconclusive as the above comparisons are, they seem to favour strongly this view as to the source of the vanadium, and in a measure are confirmatory of the observation of Hayes (*Proc. Am. Ac.*, 1875, x., 294), who, rather indefinitely, associates it with phosphorus and proto-salts of iron and manganese, which are usually more prominent components of basic than of acid rocks.

We are probably justified by the evidence in tabulating the vanadium as V_2O_3 in analyses of igneous and some metamorphic rocks which have undergone little or no oxidation; but with sandstones, clays, limestones, &c., which are of more or less decided secondary origin, this is probably not the case. The probabilities are there largely in favour of its acid character and the existence of various vanadates of calcium, iron, aluminum &c., in which case it should appear in analytical tables as V_2O_5 (see Note).

It was not until the greater part of the above tests had been finished that any careful attempt was made to identify molybdenum as well as vanadium. From the evidence gathered during the latter part of the work it would seem that molybdenum when it does occur is a much less important constituent quantitatively than vanadium, and that, unlike the latter, it accompanies the more acid rocks. Molybdenite is a well-known accessory constituent of some granites, &c., but in the above instances its amount was extremely small, and no hint was obtained as to its state of combination.

NOTE.—In the regular course of analysis vanadium will be weighed with alumina, iron, titanium, &c., since it is precipitated by both ammonia and sodium acetate in presence of those and other metals; hence the alumina percentages in nearly all rock analyses heretofore made are subject to correction for the vanadium the rock may have held. This correction is of course to be made in terms of V_2O_5, and not of V_2O_3.

All determinations of iron are likewise affected by its presence whether as V_2O_5 or V_2O_3. As V_2O_3 it will make the FeO appear too high in the proportion $V_2O_3 : 4FeO$, or 150·8 : 288, an error which becomes appreciable in some of the basic rocks, and amounts to 0·25 per cent in the biotite 23*a*. As V_2O_5 the FeO will not be affected, but in either condition the Fe_2O_3 will need correction and to a different extent, according as the titration of iron is made after reduction by hydrogen sulphide or by hydrogen. If the former is used, as should always be the case in presence of titanium, the vanadium is reduced by it to V_2O_4, which in its action on permanganate is equivalent to two molecules of FeO representing one of Fe_2O_3, or only one-half as great as the influence on the FeO titration of the same vanadium as V_2O_3. An example will make this clear:—

Found 2·50 per cent apparent FeO in a rock containing 0·13 per cent V_2O_3.
Deduct 0·25 per cent FeO equivalent in its action on $KMnO_4$ to 0·13 V_2O_3,
Leaving 2·25 per cent FeO corrected.
Found 5·00 per cent apparent total iron as Fe_2O_3 in the same rock.
Deduct 0·14 per cent Fe_2O_3 corresponding to 0·13 per cent V_2O_3,
Leaving 4·86 per cent corrected total iron as Fe_2O_3.
Deduct 2·50 per cent Fe_2O_3 equivalent to 2·25 per cent FeO,
Leaving 2·36 per cent Fe_2O_3 in the rock.

Failure to correct for the vanadium in both cases would have made the figures for FeO and Fe_2O_3 respectively 2·50 and 2·22, instead of 2·25 and 2·36 as shown above.

Chemical Method employed.

In conclusion, it is proper to outline the method by which the foregoing tests were carried out, and to indicate the precautions that must be observed in order to insure good results.

Quite a number of workers have busied themselves with the problem of vanadium estimation in ores and rocks, particularly magnetites and other iron ores, and the methods used have been often diverse in parts, if not altogether. There is nothing absolutely novel in the following, except that chromium and vanadium when together need not be separated, but are determined, the former colorimetrically, the latter volumetrically, in the same solution as detailed elsewhere (*Jour. Am. Chem. Soc.*, xx., pp. 454 and 461, 1898).

Five grms. of the rock are thoroughly fused over the blast, with 20 grms. of sodium carbonate and 3 of sodium nitrate. After extracting with water and reducing manganese with alcohol it is probably quite unnecessary, if the fusion has been thorough, to re-melt the residue as above, though for magnetites and other ores containing larger amounts of vanadium than any of these rocks, this may be necessary, as Edo Claassen has shown (*Am. Chem. Jour.*, viii., 437). The aqueous extract is next nearly neutralised by nitric acid, the amount to be used having been conveniently ascertained by a blank test with exactly 20 grms. of sodium carbonate, &c., and the solution is evaporated to approximate dryness. Care should be taken to avoid over-running neutrality, because of the reducing action of the nitrous acid set free from the nitrite; but when chromium is present it has been my experience that some of this will invariably be retained by the precipitated silica and alumina, though only in one case have I observed a retention of vanadium, it being then large. The use of ammonium nitrate instead of nitric acid for converting the sodium carbonate into nitrate did not seem to lessen the amount of chromium retained by the silica and alumina.

As a precautionary measure, therefore, and always when chromium was to be estimated also, the silica and alumina precipitate was evaporated with hydrofluoric and sulphuric acids, the residue fused with a little sodium carbonate, and the aqueous extract again nearly neutralised

with nitric acid and boiled for a few moments, the filtrate being added to the main one.

Mercurous nitrate was now added to the alkaline solution in some quantity so as to obtain a precipitate of considerable bulk, containing chromium, vanadium, molybdenum, tungsten, phosphorus, and arsenic, should all happen to be in the rock, and also an excess of mercurous carbonate to take up any acidity resulting from the decomposition of the mercurous nitrate. Precipitating in a slightly alkaline instead of a neutral solution renders the addition of precipitated mercuric oxide unnecessary for correcting this acidity. If the alkalinity, as shown by the formation of an unduly large precipitate, should have been too great, it may be reduced by careful addition of nitric acid until an added drop of mercurous nitrate no longer produces a cloud.

After heating and filtering, the precipitate is ignited in a platinum crucible after drying and removing from the paper to obviate any chance of loss of molybdenum and of injury to the crucible by reduction of phosphorus or arsenic. The residue is fused with a very little sodium carbonate, leached with water, and the solution if coloured yellow filtered into a graduated flask of 25 or more c.c. capacity. The chromium is then estimated accurately in a few minutes by comparing with a standard alkaline solution of potassium monochromate (*Journ. Am. Chem. Soc.*, 1898, xx., 454). Then, or earlier in absence of chromium, sulphuric acid is added in slight excess, and molybdenum and arsenic together, with occasional traces of platinum, are precipitated by hydrogen sulphide, preferably in a small pressure bottle.* If the colour of the precipitate indicates absence of arsenic, the filter with its contents is carefully ignited in porcelain, and the delicate sulphuric acid test for molybdenum is applied.

The filtrate, in bulk from 25 to 100 c.c. is boiled in a current of carbon dioxide to expel hydrogen sulphide, and titrated at a temperature of 70—80° C., with a very dilute solution of permanganate representing about 1 m.grm. of V_2O_5 per c.c. as calculated from the iron strength of the permanganate, 1 molecule of V_2O_5 being indicated for each one of Fe_2O_3. One or two checks are always to be made by reducing again in a current of sulphur dioxide gas, boiling this out in a current of carbon dioxide again, and repeating the titration.

As shown in a previous paper (*Journ. Am. Chem. Soc.*, 1898, xx., 464) the presence of even thirty times as much Cr_2O_3 as V_2O_5 does not prevent a satisfactory determination of the vanadium if the precautions therein given are observed, provided there is present not less than ½—1 m.grm. of V_2O_5 in absolute amount. In absence of chromium less than half a m.grm. can be readily estimated. The phosphoric acid almost invariably present does not affect the result.

In case the volume of permanganate used is so small as to make doubtful the presence of vanadium, it is necessary to apply a qualitative test, which is best made as follows:—The solution is evaporated and heated to expel excess of sulphuric acid, the residue is taken up with 2 or 3 c.c. of water and a drop or two of dilute nitric acid, and a couple of drops of hydrogen peroxide are added. A characteristic brownish tint indicates vanadium. Unless the greater part of the free sulphuric acid has been removed the appearance of this colour is sometimes not immediate and pronounced; hence the above precaution.

The above is a surer test to apply than the following:—Reduce the bulk to about 10 c.c., add ammonia in excess, and introduce hydrogen sulphide to saturation. The beautiful cherry-red colour of vanadium in ammonium sulphide solution is much more intense than that caused by hydrogen peroxide in acid solution, but the action of ammonia is to precipitate part or all of the vanadium with the chromium or aluminum that may be present or with the manganese used in titrating, and ammonium sulphide is unable to extract the vanadium wholly from these combinations. Usually, however, the solution will show some colouration, and addition of an acid precipitates brown vanadium sulphide, which can be collected, ignited, and further tested if desired.

Summary of Results.

Vanadium occurs in quite appreciable amounts in the more basic igneous and metamorphic rocks, up to 0·08 per cent or more of V_2O_3, but seems to be absent—or nearly so—from the highly siliceous ones. The limited evidence thus far obtained points to the heavy ferric aluminous silicates as its source—the biotites, pyroxenes, amphiboles. As opportunities offer, further evidence will be accumulated, and it is hoped that other chemists will lend their aid.

Limestones and sandstones appear to contain very small amounts of vanadium, as shown by analysis of a composite sample of each aggregating over 700 different occurrences.

From the few tests for molybdenum it appears as if this element were confined to the more siliceous rocks. It is present in no observed case in amount sufficient for quantitative measurement when operating on 5 grms. of material.

Note.—Since the above was written, a few tests have been made on minerals of which powdered samples were at hand. A phlogopite from Burgess, Canada, gave 0·007 per cent V_2O_3. Mica from Laurel Hill, Georgia, gave 0·026 per cent V_2O_3. Protovermiculite from Magnet Cove, Ark., gave 0·04 per cent V_2O_3. Hallite from Chester Co., Pa., gave 0·01 per cent V_2O_3. Jeffersonite, from Franklin, N.J., gave none, and a non-ferruginous amphibole from St. Lawrence Co., N.Y., gave a faint trace.

* From a sulphuric solution the separation of molybdenum by hydrogen sulphate is much more rapid and satisfactory than from a hydrochloric solution.

NOTICES OF BOOKS.

Elements of General Chemistry, with Experiments. By John H. Long. Chicago: E. H. Colegrove, Sales Agent. 1898. Pp. vi.—408. 8vo. Illustrated.

In preparing this book the author, who is Professor of Chemistry in the North-western University, has used a part of his work "Experimental and Analytical Chemistry," long since out of print, and he has added enough new matter to make of it a complete text-book of elementary general chemistry, sufficient for college students beginning the subject. In the Preface Dr. Long remarks that in too many instances the student is introduced to qualitative analysis as his first laboratory work, and this is followed by gravimetric analysis to complete a course: this plan gives the beginner a distorted idea of the relative importance of analytical chemistry in the study of the science, whereas a knowledge of the properties of a substance, the methods of its preparation, and its uses, is far more important for the beginner than acquaintance with methods of separation. On these grounds the author has introduced illustrative experiments (to the number of 174) throughout the work, and the student is advised that he should consider each experiment performed as a question, and the results obtained as the answers.

In the Introduction the student is made acquainted with the three states of matter, solution, crystallisation, precipitation, and the characteristics of physical and chemical changes, by the assistance of thirty-seven simple experiments and explanatory text; then follows the consideration of oxygen and hydrogen and their compounds; after these the elements are treated in a logical order in twenty-three chapters, concluding with the platinum group.

The illustrative experiments are well selected, and the directions for conducting them are clear, though in some cases a simple woodcut would help the student's comprehension.

A blemish in the make-up of the book, in no wise affecting its accuracy, is the fact that the running headlines remain unchanged throughout the 400 pages, whereas the odd-numbered pages ought to indicate to which chapter they belong. The work seems to be free from typographical errors, and there is an index. H.C.B.

CORRESPONDENCE.

FIXATION OF NITROGEN.

To the Editor of the Chemical News.

Sir,—Provisional Protection has recently been obtained for the manufacture of ammonia by the destructive distillation of hydrocarbons in the presence of nitrogen, relying on the nature of nascent hydrogen to combine with nitrogen.

This is simply adopting the natural process by which ammonia is formed in gas-works with the nitrogen of the coal.

The whole question of the employment of nascent hydrogen is a large one, and it is in this direction that success must be looked for.—I am, &c.,

B. Piffard.

MEETINGS FOR THE WEEK.

Thursday, Nov. 3rd.—Chemical, 8. "A Determination of the Equivalent of Cyanogen," by George Dean, B.A. "Action of Light on Platinum, Gold, and Silver Chlorides," by E. Sonstadt. "Methanetrisulphonic Acid," by E. H. Bagnall, B.Sc. "A Composite Sodium Chlorate Crystal in which the Twin Law is not followed," by W. J. Pope. "Composition of American Petroleum," by Sydney Young, D.Sc., F.R.S. "Separation of Normal and Iso-heptane from American Petroleum," and "Action of Fuming Nitric Acid on the Paraffins and other Hydrocarbons," by F. E. Francis, B.Sc., and Sydney Young, F.R.S. "Boiling-points and Specific Gravities of Mixtures of Benzene and Normal Hexane," by D. H. Jackson, M.A., and Sydney Young, F.R.S.

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ON THE SUPPOSED NEW GAS, ETHERION.

By Sir WILLIAM CROOKES, F.R.S.

IN the CHEMICAL NEWS for the 21st of October last appeared an article giving an account of "Etherion: a New Gas," by Mr. Charles F. Brush. This was only an abstract of the complete paper read by Mr. Brush before the American Association for the Advancement of Science, at Boston, on August 23, and it would not be right to enter into detailed criticism of the results claimed by the author until his complete paper is available. I may, however, be permitted to bring forward some old researches, published and unpublished, which tend, in my opinion, to show that the new gas, Etherion, may be nothing more than aqueous vapour.

Dating from my early work on "Repulsion resulting from Radiation," I noticed in 1873* that a little aqueous vapour thrown into the vacuum converted into attraction the repulsion due to radiation. I worked on this subject for some years, and in 1876† I was experimenting on the effect of radiation exerted by the flame of a candle on discs of pith at the ends of a light torsion beam suspended in a vacuum by means of a delicate silk fibre. The disc at one end of the beam was coated with lamp-black, and the disc at the other end was left in its natural state. The observations bearing on the action of aqueous vapour are quoted from the paper itself:—

"During the exhaustion of one of these pieces of apparatus, an action of aqueous vapour was observed which explained some of the anomalies I had met with in the course of this investigation. The apparatus had a little water in it; and although the mercury pump brought the gauge to within about 8 m.m. of the barometric height in the course of ten minutes, the tension of the aqueous vapour prevented it from rising higher. After working the pump for several hours, and gently warming the different parts of the apparatus, the liquid water was evaporated, and only aqueous vapour remained. The gauge now rapidly rose to the height of the barometer, the apparatus necessarily being filled with the residual aqueous vapour. On bringing a lighted candle near the discs, I expected to see the black one violently repelled; but instead of that the connecting arm set equatorially, showing that the radiation from the candle within a few inches of the discs repelled the white one as strongly as it did the black. The pump was kept in action, and oil of vitriol was passed through it once or twice. This was continued for about four hours, and on testing the apparatus from time to time with a candle the repulsion of the black disc gradually increased, the arm setting at a greater and greater angle from the equatorial position, but at no time getting very strongly deflected. An accident happening to one of the tubes of the pump, it was necessary to let air into the apparatus; it was passed in slowly over oil of vitriol. As soon as the pump was mended, exhaustion of the apparatus was re-commenced. As soon as the gauge rose within 6 m.m. of the barometric height, the candle was seen to repel the black disc. At 3 m.m. the superior repulsion of the black over the white disc was sufficient to cause the arm to set 45°; and as the exhaustion got better, the repulsion of the black disc increased, until—at the point where the gauge and barometer were level—the candle exerted a strong action many feet off, and when brought close to the instrument set the bar and discs in most violent agitation—the black disc being driven violently away, and the connecting arm swinging rapidly on each side of the axial position. This experiment shows that the presence of even a small quantity of aqueous vapour in the exhausted apparatus almost—if not quite—neutralises the more energetic action which luminous rays appear to exert on a blackened surface. In the first case, even when the gauge and the barometer were appreciably level, and the pump had been working for some hours, the superior repulsion of the black over the white was not so strong as it was in the second case when the gauge was several m.m. below the barometer."

Soon after the above experiments were tried, the radiometer was discovered, and in June, 1886, I wrote,* that if residues of gases other than air were in the radiometer the phenomena of repulsion were different in degree, although similar in kind. Thus aqueous vapour was found to retard the force of repulsion to a great extent, and carbonic acid acted in a similar though less degree.

In 1881 I entered more fully into the retarding effect of water vapour on the repulsion due to radiation on bodies free to move in different gases at high vacua, and, in a paper on "The Viscosity of Gases at High Exhaustions," I wrote† :—

"The presence of water vapour (in air) shows itself in the very slight amount of repulsion produced by radiation. Repulsion commences in air at a pressure of 12 m.m., whilst at a higher exhaustion the maximum effect rises to over forty divisions. Here, however, repulsion, does not begin till the exhaustion is higher than the barometer gauge will indicate, whilst the maximum action after long-continued pumping is only nine divisions. This confirms the results frequently met with in my researches on "Repulsion resulting from Radiation," where the presence of even a trace of aqueous vapour was found to have a strong action in diminishing the sensitiveness of the radiometer and other instruments."

"I was unable to take pressures after 1·0 m.m. as the McLeod measuring apparatus does not give trustworthy indications when aqueous vapour is present. As soon as the pressure in the measuring tube rises above the tension of aqueous vapour, water condenses in it, and measurements can no longer be taken."

I give these extracts to show that the anomalous action of aqueous vapour had been obtruding itself on my notice since 1878. With the object of ascertaining more definitely what this action was, in 1880 I commenced some experiments on heat conduction in air and other highly rarefied gases. Of this research only the first part was published, namely that referring to the conduction of heat across a space containing highly rarefied dry air. The experiments in hydrogen, aqueous vapour, and other gases are still unpublished. It is from the results obtained with these gases that I am led to believe that etherion will turn out to be water vapour. In coming to this conclusion I can obviously only argue on the few pieces of evidence given by Mr. Brush in the abstract before me;‡ when the complete paper comes to hand it may contain other evidence, for it is unlikely that the author would announce so important a discovery on the doubtful evidence at present given.

The properties of etherion, given in the abstract, are as follows:—It is presumably elementary, and is a constituent of the atmosphere. It has enormous heat-conductivity at very low pressures, ranging from nearly as good as hydrogen at a pressure of 36 millionths of an atmosphere, to twenty-seven times as good as hydrogen at 0·38 of a millionth. It is absorbed from the atmosphere by glass and is evolved by heating the glass in vacuo, being re-absorbed on cooling. It is also absorbed by phosphorus

* *Phil. Trans.*, vol. clxiv., Part 2, pp. 515-517.
† *Phil. Trans.*, vol. clxvi., Part 2, p. 329.

* *Proc. R. S.*, vol. xxv., No. 172, p. 140.
† *Phil. Trans.*, vol. clxxii., Part 2, p. 428.
‡ CHEMICAL NEWS, vol. lxxviii., p. 197, Oct. 21. 1898.

pentoxide and by soda-lime; on this account no desiccating agent could be used.

For the following reasons I consider etherion to be water vapour:—

Firstly, as to its absorption by glass and the evolution of the gas on heating the glass in a vacuum. I must begin with a quotation from a paper I wrote in 1879, "Contributions to Molecular Physics in High Vacua."*

"I have already mentioned that platinum will fuse in the focus of converging molecular rays projected from a concave pole. Another piece of apparatus was constructed in which a plate of German glass was held in the focus of the molecular bombardment. The vacuum was so good that no hydrogen or other lines could be seen in the spectrum of the emitted light. The focus was now allowed to play on the glass, when the glass soon became red-hot. Gas appeared in the tube, and hydrogen lines now were visible in the spectrum. The gas was pumped out until hydrogen disappeared from the spectrum. It was now possible to heat the glass to dull redness without hydrogen coming in the tube; but as soon as the heat approached the fusing-point, the characteristic lines appeared. It was found that however highly I heated the glass, and then pumped the tube free from hydrogen, I had only to heat the glass to a still higher temperature to get a hydrogen spectrum in the tube. I consider the hydrogen spectrum comes from vapour of water, which is obstinately held in the superficial pores, and which is not entirely driven off by anything short of actual fusion of the glass. The bubbles noticed when the disintegrated and fused surface of the tube was examined under the microscope are probably caused by escaping vapour of water. A piece of glass from a tube which had cracked at incipient fusion was examined under the microscope. The surface appeared curiously crumpled up and filled with minute bubbles, as if the glass had been boiling."

I have repeated the above-described experiment in a slightly modified form, using as a source of vapour or gas powdered glass which had been for some time exposed to the air.

A vacuum tube was made with a narrow tube connecting the end bulbs carrying the poles, in such a way that the spectrum could be examined "end on." At one part a supplementary tube was attached, containing about 10 grms. of powdered soda-glass. The phosphoric drying tube had been removed from the pump, and the apparatus was exhausted. The powdered glass was then gently heated in a vessel of hot water, when the gauge sank to about 9 m.m. and remained there for some time. The spectrum of the gas showed water vapour very strongly, a trace of nitrogen, and a little carbonic acid. Exhaustion was continued until the gauge rose to ½ m.m., when the glass powder was again heated a little more than at first. The gauge again sank to 9 m.m., and the spectrum showed the same gaseous mixture as before. Again heat was applied to the powdered glass, the gauge was depressed, and the pump set going. This was repeated several times, the last few spectroscopic testings showing nothing but water and carbonic acid. Finally, after thorough exhaustion, the powdered glass was heated strongly until the tube and powder melted together, and the gauge sank about 4 m.m. The spectroscope again showed water and carbonic acid, and continued so to do until all the gas had been pumped out.

This experiment, corroborating the one of 1879, proves that air-dry glass condenses on its surface a considerable quantity of water and carbonic acid which does not come off in a vacuum until heat is applied. After a sufficient amount of water vapour to show itself spectroscopically has been driven off, and a non-conducting vacuum again formed, a further increase of temperature will drive off a fresh quantity of water, and the alternations of exhausting and driving off water can be performed many times, the temperature being each time raised higher and higher until the bulb collapses. No line was seen in any of the spectra which could be ascribed to an unknown gas; none but those of water and carbonic acid being observed.

Secondly, as to the conductivity for heat of gases and vapours other than air, I will first give briefly some results of my unpublished work on this subject.

Dry hydrogen at atmospheric pressure is a much better conductor for heat than is air, but this superiority falls off as the pressure diminished, and at a high exhaustion air and hydrogen are about equal. Carbonic acid is a worse conductor than air at all pressures.

Starting with water in the thermometer apparatus, and then pumping until only a just visible trace of liquid water was left, and the gauge was steady at 9 m.m., the conductivity for heat was close upon that of air at the ordinary pressure. Continuing exhausting until all visible water had disappeared, and the gauge commenced to rise above 9 m.m., the conductivity diminished, and at the higher exhaustions, when the gauge and barometer are apparently on a level, the conductivity of the residual vapour was still less, although not so great as that of air or hydrogen. At the highest exhaustion I could get after the pump had been going for some hours,* the thermometer in the bulb required 295 seconds to rise 25°. At similar high vacua with air the time required to rise 25° was 491 seconds, and with a hydrogen vacuum the time required was 441 seconds.

These experiments, of which only the results are here given, show that at high vacua water-gas is a better conductor than either air or hydrogen at similar pressures.

But Mr. Brush gives as the most remarkable property of etherion its heat conductivity, which is 27 times that of hydrogen at a pressure of 0·38 of a millionth of an atmosphere. Now it has been found that as water-gas is rarefied its heat conductivity diminishes in a greater ratio than that of hydrogen. At the time I tried these experiments I could not conveniently obtain or measure pressures below 1 millionth, but at these high vacua water-gas gains so rapidly on hydrogen, that I am prepared to believe that at Mr. Brush's low pressure of 0·38 millionth the ratio may even be as great as that he ascribes to etherion.

Within the last few days I have repeated the experiment with the thermometer in the bulb with which the foregoing experiments were tried, but using powdered soda glass as a source of gas. The phosphoric acid drying tubes were removed, and the apparatus was well exhausted. The glass was at first gently heated and the evolved gas pumped out. This was repeated several times, until at last, after very strongly heating the tube of glass powder until it melted, it was sealed off, and observations were taken of the heat conductivity of the residual gas. The time occupied in the thermometer sinking 25° C. at the various degrees of high exhaustion were very near those for water vapour, and the conductivity fell off as pressure diminished more closely according to the water curve than the hydrogen curve. The falling off was not, however, quite so great as when pure water was used. This I ascribe to the presence of carbonic acid, which is always evolved, with water, when glass is strongly heated in a vacuum.

As I have already said, I have no wish to speak at all positively on a paper of which only an abstract, probably an imperfect one, is to hand. But on the evidence at present available I consider it more probable that etherion is water vapour than that it is a new elementary gas, and this is corroborated by the observations made by Mr. Brush, that etherion is absorbed by phosphoric acid and soda-lime, as well as by the powdered glass from which it has previously been driven off by heat.

* *Phil. Trans.*, vol. clxx., Part 2, pp. 658, 659.

* I cannot use the McLeod gauge with aqueous vapour, owing to its condensing in the pressure tube.

AN EXAMINATION OF THE PRODUCTS OBTAINED BY THE DRY DISTILLATION OF BRAN WITH LIME.

By W. F LAYCOCK, Ph.D.

(Concluded from p. 212).

Examination of B.

THE black oil weighed 420 grms. On twice distilling, 220 grms. of oil* boiling between 70—325° passed over, and about 200 grms. of tar remained in the still. The distillate was shaken with 200 c.c. of 5 per cent hydrochloric acid. The acid solution, which was of a dark red colour, was separated from the oil, and the latter washed with small quantities of water until free from acid. The acid extract and the washings were subsequently mixed and filtered from a little resinous matter. On treating the filtered solution with excess of sodium hydrate, a black oil separated out, and was extracted with ether. The aqueous residue was distilled with steam. No aldehyds were detected in the distillate on testing with ammoniacal silver nitrate and decolorised magenta solutions.

The ethereal extract was evaporated, and the remaining oil distilled. About 23 grms. of a yellow oil, boiling from 70—290° and containing 13 per cent of nitrogen, was obtained. It was boiled with excess of hydrochloric acid for some hours, and, after filtering from a little pyrrol-red, the saline solution was evaporated to dryness on the water-bath. The dark crystalline mass which remained was distilled with excess of solid caustic potash in an oil bath. The distillate was dissolved in ether, dried with solid caustic potash, and, after evaporation of the ether, distilled. About 10 grms. of oil passed over; it boiled from 80—270°, and was free from pyrrol. It contained no aniline, but an amido-compound was evidently present, as a red colouration was obtained on adding a drop to a solution of furfurol and glacial acetic acid. In order to destroy amido-compounds, concentrated nitric acid was added to the oil in the cold. The red-brown solution was afterwards heated on the water-bath, poured into water, and distilled with steam. A small quantity of a heavy dark yellow oil (evidently a nitro-compound) passed over. The acid residue, after filtration, was saturated with 100 grms. of solid caustic potash, the oil which separated being extracted with ether, and the ethereal extract dried with caustic potash. On evaporation of the ether and subsequent distillation, 7 grms. of almost colourless oil resulted. The oil possessed the characteristic smell of pyridine, had a very bitter taste, and was strongly alkaline to litmus paper. White fumes were produced when vapour of hydrochloric acid was brought near it. The oil was fractionated twice, 10 fractions being taken between 140° and 250°. The greater part passed over at 165—185°. Each portion gave reactions with solutions of iodine in potassium iodide, tannic acid, picric acid, and mercuric chloride. Potassium ferrocyanide gave precipitates with several fractions. No distinct colourations were obtained with concentrated mineral acids. The fractions between 185° and 250° each contained 12·5 per cent nitrogen. The remaining fractions gave the following results :—

175—185° .. 0·1052 gave 11·6 c.c. moist nitrogen at 13° and 749 m.m.
165—175° .. 0·1171 gave 13·3 c.c. moist nitrogen at 15° and 749 m.m.
155—165° .. 0·1265 gave 15·3 c.c. moist nitrogen at 15·5° and 742 m.m.
140—155° .. 0·1991 gave 24·1 c.c. moist nitrogen at 16·5° and 741·5 m.m.

* The last drops gave a brilliant red colour on boiling with a pine splinter and dilute hydrochloric acid. Bromine acted violently on the oil, white fumes being produced, and on the excess of bromine being removed by a current of air, the mixture assumed an intense violet colour.

Fraction.	Nitrogen.	Calculated for—	
175—185°	12·84 per cent	collidine $C_8H_{11}N$	11·57 per cent
165—175°	13·10 „	lutidine C_7H_9N	13·09 „
155—165°	13·78		
140—155°	13·75 „	picoline C_6H_7N	15·05 „

Analyses of various fractions of bases obtained in a similar manner from a different sample of bran gave the following results :—

180—200° .. 0·0916 gave 0·2632 CO_2 and 0·0780 H_2O.
0·0833 gave 8·6 c.c. moist nitrogen at 18·5° and 767·2 m.m.
170—180° .. 0·0890 gave 0·2555 CO_2 and 0·0746 H_2O.
0·1725 gave 0·4906 CO_2 and 0·1433 H_2O.
0·0713 gave 7·41 c.c. moist nitrogen at 15·5° and 751·7 m.m.
160—170° .. 0·0930 gave 0·2675 CO_2 and 0·0770 H_2O.
0·1644 gave 0·4746 CO_2 and 0·1304 H_2O.
0·1690 gave 18·4 c.c. moist nitrogen at 15° and 734·3 m.m.
140—160° .. 0·1747 gave 0·4918 CO_2 and 0·1370 H_2O.
0·1626 gave 0·4560 CO_2 and 0·1252 H_2O.
0·1461 gave 16·0 c.c. moist nitrogen at 15·5° and 762·7 m.m.
0·1161 gave 13·4 c.c. moist nitrogen at 15·5° and 737 m.m.

	Fraction 180—200°.	Fraction 170—180°.		Calculated. $C_8H_{11}N$.
C	78·35 per cent	78·26	77·56 per cent	79·34
H	9·46	9·31	9·23	9·09
N	12·08	12·00	—	11·57

	Fraction 160—170°. I.	Fraction 160—170°. II.	Calculated. C_7H_9N.
C	78·43	78·72	78·50
H	9·20	8·83	8·41
N	12·30	—	13·09

	Fraction 140—160°.* I.	Fraction 140—160°.* II.	Calculated. C_6H_7N.
C	76·79	76·48	77·42
H	8·72	8·57	7·53
N	12·90	13·06	15·05

* This fraction was evidently not perfectly dry.

Several fractions were acidified with concentrated hydrochloric acid, an excess of a concentrated solution of platinum tetrachloride added, and the solution allowed to evaporate spontaneously. When the crystals ceased to increase in bulk, the mother-liquor was decanted, the crystals were washed with alcohol and ether, and dried at 100°. On analysis the platinum salts gave the results recorded in Table III.

200—225° gave a picrate as yellow microscopic arborescent crystals melting at 190—192°. The figures in this table conclusively prove the basic oil to contain picoline, lutidine, and collidine.

Treatment of the Non-basic Oil.

The oil which was unaffected by dilute hydrochloric acid weighed 173 grms. It yielded on distillation 166 grms. of oil boiling at 86—310°, about 145 grms. passing over between 150—280°; it contained 2 per cent nitrogen.* Bromine acted violently on the oil, white fumes (giving an acid reaction with litmus paper), a violet coloration, and a dark brown oil being produced. The whole of the oil was shaken several times with a solution of sodium bisulphite, and subsequently washed with water. The bisulphite extract was filtered, saturated with potassium carbonate, and the oil which separated extracted with ether. After drying and evaporating the ether, 4·5 grms. of oil boiling at 90—225° resulted on distilling. About 3·5 grms. dis-

* Calculated as trimethylpyrrol would be about 15 per cent.

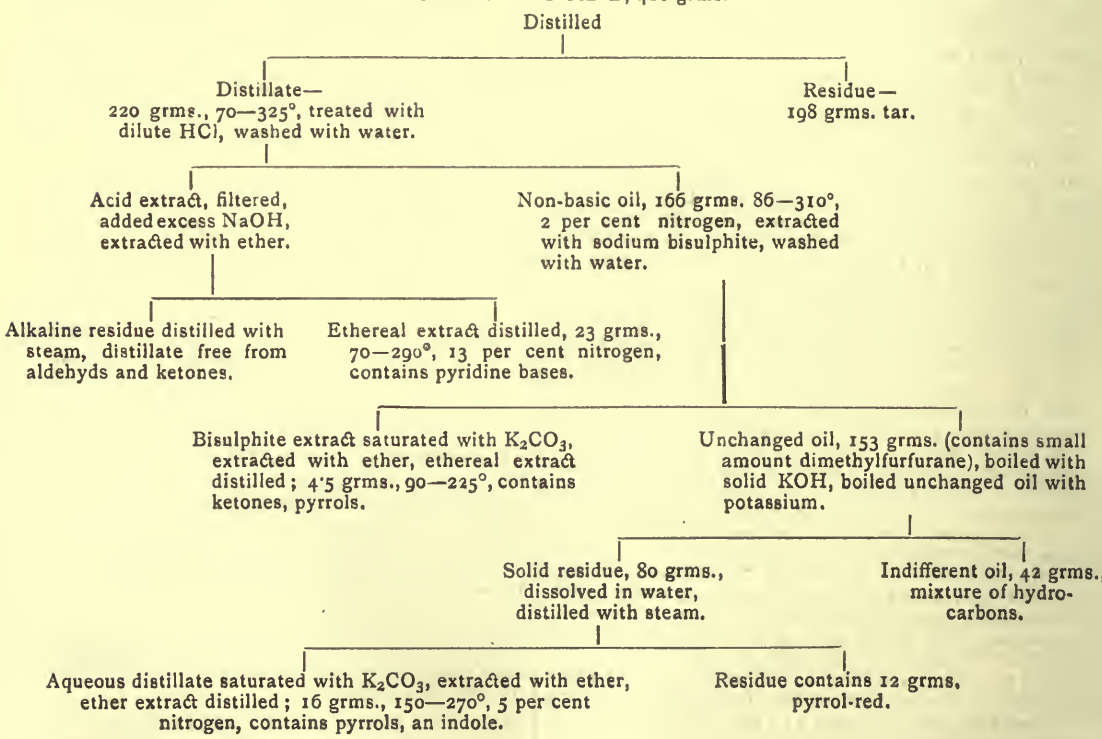
TABLE III.

Fraction 200—205° .. .. 0·1692 gave on ignition 0·0521 metallic platinum.
„ 165—175° .. .. 0·2037 „ „ 0·0641 „ „
„ 155—165° .. .. 0·1630 „ „ 0·0529 „ „

Fraction.	Pt salt.	Melting-point.	Platinum found.	Per cent Pt calculated.	
200—205°	Red-brown dense masses of thick needles, silky lustre	190—191° decomposes.	30·79	30·12 $(C_8H_{11}NHCl)_2PtCl_4$.	(1)
165—175°	Dense masses of orange-red needles and square plates	181—183° decomposes.	31·47	31·47 $(C_7H_9NHCl)_2PtCl_4$.	(2)
155—165°	Similar to preceding fraction . ..	191—193° decomposes.	32·45	31·99 $(C_6H_7NHCl)_2PtCl_4H_2O$.	(3)
140—155°	Orange-red thick needles and square plates	185°	—	—	(4)

(1) α-Methylethylpyridine platinochloride melts at 190°.
(2) α-Ethylpyridine platinochloride melts at 164°.
(3) β-Picoline platinochloride (hydrated salt) melts at 191—195°.
(4) α-Picoline platinochloride melts at 178°.

TABLE IV.—THE OIL B, 418 grms.


Distilled
Distillate— 220 grms., 70—325°, treated with dilute HCl, washed with water.
Residue— 198 grms. tar.
Acid extract, filtered, added excess NaOH, extracted with ether.
Non-basic oil, 166 grms. 86—310°, 2 per cent nitrogen, extracted with sodium bisulphite, washed with water.
Alkaline residue distilled with steam, distillate free from aldehyds and ketones.
Ethereal extract distilled, 23 grms., 70—290°, 13 per cent nitrogen, contains pyridine bases.
Bisulphite extract saturated with K_2CO_3, extracted with ether, ethereal extract distilled; 4·5 grms., 90—225°, contains ketones, pyrrols.
Unchanged oil, 153 grms. (contains small amount dimethylfurfurane), boiled with solid KOH, boiled unchanged oil with potassium.
Solid residue, 80 grms., dissolved in water, distilled with steam.
Indifferent oil, 42 grms., mixture of hydrocarbons.
Aqueous distillate saturated with K_2CO_3, extracted with ether, ether extract distilled; 16 grms., 150—270°, 5 per cent nitrogen, contains pyrrols, an indole.
Residue contains 12 grms. pyrrol-red.

tilled between 125° and 215°. It contained 5·5 per cent nitrogen. Potassium acted violently on the oil. The solid product of the reaction was washed with ether and dissolved in water. The aqueous solution, on distillation, yielded a colourless oil which gave a well marked pyrrol reaction, and a white precipitate with mercuric chloride. Phenylhydrazin mixed with the oil became warm, and water separated on standing. A few drops of the oil, collected during the distillation at about 100°, gave a brilliant coloration with Bittó's reagent for methylpropyl ketone, and a violet coloration with a pine splinter and hydrochloric acid proved the presence of a homologue of furfurane.

The oil unaffected by sodium bisulphite weighed 153 grms. A portion of oil obtained in a similar manner from a former distillation of bran was proved in the following manner to contain dimethyl furfurane:—

100 grms. of oil, 1000 c.c. water, and 25 grms. of concentrated hydrochloric acid were heated in sealed tubes at 160° for six hours. The insoluble oil was filtered, and the claret-coloured filtrate saturated with potassium carbonate. A small quantity of a brown oil, smelling of acetonyl acetone, separated and was extracted with ether. The ethereal solution was dried with potassium carbonate, the ether evaporated, and the remaining oil distilled. About 0·6 grm. of nearly colourless oil boiling at 170—

195°, mostly at 185—190°, passed over.* This portion was mixed with 0·8 grm. potassium carbonate and 0·8 grm. hydroxylamine hydrochloride and dissolved in the least possible quantity of warm water for solution. Crystals separated on allowing the solution to stand. A small quantity of brown oil being also present, the whole was warmed until the crystals dissolved, and the oil filtered off; the latter gave a strong pyrrol reaction. The crystals which were deposited from the filtered solution were recrystallised from a small quantity of water; the purified crystals were in clusters and just tinged pink. After filtration and drying on the water-bath, 0·17 grm. of crystals melting at 132—133° were obtained.†

0·1404 gave 23·3 c.c. moist nitrogen at 16° and 757·2 m.m.

Nitrogen, 19·27 per cent $C_6H_{12}N_2O_2$. Calculated, 19·45 per cent N.

Treatment of the Oil which was Unchanged by Sodium Bisulphite.

An attempt was made to separate the pyrrols in the form of potassium salts from the oil unaffected by sodium bisulphite, by long-continued boiling with solid caustic potash. Ammonia was evolved, and the oil several times decanted from the brown solid products and treated with more potash. When no further action took place the oil was boiled repeatedly with potassium. The solid products of the reactions were separated from the fused potash and the potassium respectively. They amounted to about 80 grms., and after washing with ether constituted a brown powder which took up moisture with avidity and quickly became oily. The mass was dissolved in water and distilled with steam. The residue in the still gave on filtration about 12 grms. of pyrrol red. The aqueous distillate mixed with oil was extracted with ether. About 16 grms. of oil boiling at 150—270° resulted. The portion boiling at 150—160° contained 5 per cent nitrogen. The oil was found to be a mixture containing pyrrols and indols, as, besides having the characteristic smell of the latter, it gave Beyer's reaction for indole. Various fractions of the oil were tested separately, and the lower ones gave the following reactions for pyrrols:—Boiling with a solution of isatine in glacial acetic acid caused a blue colouration: phenanthraquinon in glacial acetic acid gave a violet colouration on adding dilute sulphuric acid and chloroform. The last drops from the distillation at about 270° did not give these colourations, but exhibited Fischer's pine-splinter reaction for indole.

The oil which was unaffected by potassium was washed with dilute hydrochloric acid and dried. It still contained 1 per cent nitrogen, and gave a red colour on boiling with a pine-splinter and hydrochloric acid. On distilling, 2 grms. boiled at 80—150° and 40 grms. at 150—300°. The portion boiling at 80—150° yielded on nitration a heavy yellow oil, resembling in smell and appearance nitrobenzol, which, on reducing with tin and hydrochloric acid, gave the reactions for aniline. Ten grms. of fraction 150—300° were dissolved in ether, and excess of bromine added in the cold. A few white fumes were given off. A violet coloration was produced, and the solution turned brown later. After washing out the excess of bromine with dilute sodium hydrate solution, the oil (weighing 16 grms.) was distilled with steam. The aqueous distillate contained a heavy yellow oil, which, on extraction with ether and subsequent drying, weighed 8·5 grms. It had a fragrant smell and distilled with partial decomposition at 185—235°.

The remaining 30 grms. of fraction 150—300° was shaken with cold concentrated sulphuric acid. No rise of temperature was noted. After standing twenty-four hours, the mixture was gently heated on a sand-bath, using a reversed condenser. Sulphur dioxide was evolved and carbon separated. The mass was distilled with steam and the insoluble oil which passed over extracted with ether, dried, and, after evaporation of the latter, treated with Nordhausen sulphuric acid until no further action. The unchanged oil was washed, dissolved, in ether, dried, and distilled. About 3 grms. of a mobile colourless oil, smelling like petroleum, distilled over between 190—275°; the specific gravity at 21° was 0·77. From these reactions it is evident the 42 grms. of indifferent oil consisted for the greater part of olefines mixed with paraffins and aromatic hydrocarbons. (See Table IV.).

Summary of Results.

The following substances were separated from the aqueous distillate:—

A.

About 300 grms. of ammonia as chloride.
" 20 " amine bases as salts (methylamine, ethylamine, and trimethylamine).
" 26 " oil containing pyrrol and its homologues (and averaging 11 per cent nitrogen).
" 29 " ketones (methylpropyl ketone) and small quantities of ethyl alcohol.
Traces of furfurans, pyridine bases, and indoles.

The Oil B yielded:—

About 10 grms. of pyridine bases (picoline, lutidine, collidine) and small quantities of amido compounds.
Small amounts of ketones and dimethyl furfurane.
16 grms. of pyrrols mixed with an indole.
42 grms. of indifferent oil, consisting chiefly of olefines and lesser quantities of paraffins and aromatic carbons.

The substances obtained by the extraction of bran with ether and other solvents are now being investigated.

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* Acetonylacetone boils at 188°.

† Acetonylacetone dioxime melts at 135°. The above method of Paal (*Ber.*, xviii., 59) for the determination of dimethylfurfurane by splitting the furfurane ring by means of dilute acid, and the formation of the dioxime from the resulting γ-diketone is applicable to other homologues of furfurane (Laycock, "Inaug. Diss.," Würzburg, 1889).

SODIUM CHLORIDE AT HIGH TEMPERATURES.

By ROBERT MELDRUM, F.C.S.

Some years ago a series of experiments was made in connection with the production of salt vapour, during which I observed that the molten salt was sometimes faintly alkaline, and that the vapour had nearly the same smell as strong hydrochloric acid, but not quite so pungent. This could not be accounted for otherwise than by assuming that the salt underwent decomposition in the absence of aqueous vapour. To settle this question the following experiments were made, which seem to demonstrate that sodium chloride in the absence of water does not form any alkali, even in the presence of the substances enumerated below, with the exception of iron peroxide:—

1. Pure NaCl, kept molten for five minutes over blowpipe, when cold, boiled out with alkali-free distilled water, which gave a distinct alkaline reaction with phenolphthalein.

2. Four grms. of the unfused salt, dissolved in 20 c.c. water, gave slight alkaline reaction.

3. Saturated 5 grms. of the unfused NaCl with pure HCl, so as to neutralise any alkali present, expelled acid by heating, and melted over blowpipe in platinum crucible. The cold fusion was extracted with alkali-free water, a distinctly alkaline reaction being the result.

4. Two samples of commercial salt were melted, but yielded a neutral solution.

5. Ten grms. of pure NaCl were saturated with pure HCl, dissolved in NH_3-free water, boiled, and evaporated to dryness; repeated this till no result was given with

methyl-orange. Finally, evaporated to dryness, and melted for fifteen minutes in platinum crucible in muffle, and when cold extracted the mass, but gave no trace of alkali. This was repeated several times with the same result.

6. Eight grms. pure NaCl + 8 grms. clay, fused in platinum crucible in muffle at white heat. The resultant mass on treatment with water gave no indication of alkali.

7. Fused 8 grms. NaCl + 8 grms. Fe_2O_3 (both alkali-free) over blowpipe in platinum crucible; distinct reaction for alkali.

8. A mixture of 8 grms. NaCl + 8 grms. Fe_2O_3 (both pure and alkali-free), fused in clay crubible in muffle for two hours at yellow heat; no trace of alkali. In this case the crucible was found, after boiling in water, to be lightly glazed inside, thus showing an action had taken place, and that the free alkali had been absorbed by the clay.

9 Fused 8 grms. NaCl + 8 grms. SiO_2 (both pure and alkali-free) in clay crucible in muffle. No trace of alkali present. On boiling the crucible it showed no evidence of having been glazed inside. However, any alkali liberated may have combined with the SiO_2 to produce a neutral salt. The same experiment repeated in a platinum crucible gave the same result.

10. When 8 grms. NaCl + 8 grms. pure plumbago dust were submitted in muffle to a white heat, the fused mass, on extracting with water and filtering, gave no result for traces of alkali.

11. Melted common salt and MnO_2 in platinum crucible over blowpipe. Fusion gave no reaction with phenolphthalein, or indication of the presence of manganates or permanganates.

12. When salt is kept molten at white heat in covered clay crucible for some hours, there is always evolved a dense white vapour which smells very like strong HCl gas, but does not act upon moist blue litmus-paper, and the melt gives no indication of alkali. The crucible when broken up and boiled showed no internal glaze. From this I assume that salt vapour has nearly the same smell as HCl.

THE COLOUR OF SULPHUR VAPOUR.*

By JAS. LEWIS HOWE and S. G. HAMNER.

Our attention was some time since called to a curious difference of opinion on the part of chemical authorities as to the colour of sulphur vapour. In twenty-nine standard text-books and reference books examined which mention the colour of the vapour, thirteen different colours are given, as follows:—

	Authorities.
Deep yellow	4
Orange	5
Orange to dark yellow	1
Orange-yellow	2
Brownish yellow	6
Yellowish brown	1
Amber	2
Yellowish red	1
Red	1
Deep red	2
Deep red to brown	1
Brownish red	2
Reddish brown	1

In no work was any mention found of a change in the colour of the vapour with changing temperature.

In order to examine the true colour of the vapour a number of experiments were carried out, which, while not complete or entirely satisfactory, nevertheless throw some light on the discrepancies cited. The first apparatus used consisted merely of a small test-tube of hard glass, within a larger tube, also of hard glass, the smaller tube being held free from contact with the larger by means of a wire frame. The ends of both tubes were stopped with asbestos wads to prevent free circulation of the air. A piece of roll sulphur was placed in the inner tube and heated by Bunsen burners. The pure sulphur vapour could be seen in the inner tube, the hot air in the outer tube preventing the condensation of the vapour on the sides. This simple apparatus gives a good view of sulphur vapour up to the softening point of the glass. The second form of apparatus used was a porcelain tube 2 c.m. in diameter and 16 c.m. long, with the ends covered by thin sheets of mica, and the whole tightly packed in a larger iron tube by clay. The inner tube was thus not sealed perfectly, but permitted the escape of the excess of sulphur vapour on heating, though under some considerable pressure. The apparatus was heated in a muffle whose rear end was replaced by a sheet of mica. It was thus possible to have a clear view through the tube while it was heating. The temperature was gauged approximately by tubes of silver chloride (melting-point 457°), lead chloride (melting-point 498°), and potassium iodide (melting-point 634°).

In every case the sulphur, when just beginning to boil, gave a vapour which would perhaps be denominated orange-yellow. This colour is almost exactly matched by a normal solution of potassium bichromate. As the temperature increases the colour very rapidly deepens, and loses every vestige of the yellowish tint. This corresponds to a temperature not much above 457°. On raising further the temperature, the colour deepens further. The deepest colour was found, by several experiments, to be at the temperature of about 500° (lead chloride just fused). The paler red colour is matched by a solution consisting of—

	Parts.
Ferric chloride (normal solution)	1
Potassium thiocyanate (normal solution)	2
Water	312

The deepest red is matched by a solution—

	Parts.
Ferric chloride (normal solution)	1
Potassium thiocyanate (normal solution)	2
Water	250

This is as far as the changes can be observed in the test-tubes. Heated in the muffle, immediately above 500°, the vapour begins to grow perceptibly lighter, at 634° being almost straw-colour. Up to this temperature the escaping jet of sulphur vapour indicated that the tube must be filled with sulphur vapour. When this jet ceased the results became too doubtful to record. That the rapidly decreasing intensity of colour was not due merely to decreasing pressure is evidenced by the fact that the colour of the vapour at its darkest point was almost exactly the same in the porcelain tube and in the test-tube, in the latter case the vapour being practically at atmospheric pressure.

The cause of the different colours applied to sulphur vapour is doubtless due to three causes:—

1. The general difficulty of describing the colours of vapours, the relative intensity of which is so much less than that of our ordinary standards.

2. The fact that the colour of sulphur vapour varies with the temperature.

3. Sulphur vapour condenses so readily that when boiled in a test-tube the sides of the tube are covered with a layer of the brownish-red liquid, which has doubtless sometimes been mistaken for the vapour. Similarly, when sulphur fumes escape from a hot covered crucible into which sulphur has been thrown, it is the condensing sulphur mist, very deep red in colour, which one sees, and not the true vapour of sulphur.

* Read at the Boston meeting of the American Chemical Society, August, 1898. From the *Journal of the American Chemical Society*, vol. xx., No. 10.

The conclusions of this paper are that the colour of sulphur vapour varies with the temperature, being of an orange tint just above its boiling-point, deepening to a red which is strongest at 500°, and then becoming rapidly lighter with increasing temperature. The colour at the boiling-point is that of a normal solution of potassium bichromate; that of the deepest red is that of a rather dilute solution of ferric thiocyanate.

It is hoped it may be possible to carry these experiments further, but no reservations are made of the subject if others are interested.

THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.*

By W. F. HILLEBRAND.

Introduction.

HAVING occasion to analyse a number of highly titaniferous magnetites containing chromium, phosphorus, and vanadium, it became a serious problem to effect satisfactory separations of all these bodies in a form fit for separate determinations. The method of T. Fischer ("Inaugural Dissertation," Rostock, 1894)—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead meta-vanadate remaining quite unattacked, according to the author, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The time required is considerable, hence it was desirable to devise a more rapid way for determining both chromium and vanadium without resorting to this separation. That this object has been measurably achieved, with certain limitations as to vanadium, the work thus far done seems to indicate. The present paper will deal only with the rapid estimation of chromium either in absence or presence of any or all of the elements above mentioned.

In view of the high colouring power of the chromates, it is surprising that this property does not seem to have been made the basis for a quantitative method for the estimation of chromium. A search through some of the more important text-books has revealed no reference to such a method, and I am unaware that one has even been suggested. Yet the results attainable by colorimetric comparisons of dilute alkaline solutions of unknown strength with those of a known standard, leave little to be desired in point of quantitative accuracy.

As with colorimetric methods in general, this one gives better results with small than with large percentages of chromium, yet it can be applied in the latter cases with very fairly satisfactory results by making a larger number of consecutive comparisons with the same solution.

Outline of Method.

The chromium is brought into a measured volume of solution as monochromate, rendered alkaline by sodium carbonate, and the whole or a portion of this solution is then compared with a definite amount of a somewhat stronger standard likewise made alkaline with sodium carbonate. The latter is diluted with water till both seem to be exactly alike in colour, when a simple calculation gives the amount of chromium sought. The actual comparison takes little time, and any number of repetitions can be made if desired in order to secure greater accuracy from the mean of a large number of observations. The preparation of the solution to be tested offers nothing novel, but certain precautions have to be observed therein as well as in the colour comparisons, which will be touched upon later.

Testing of Method by Comparison of Standard Solutions.

Two standard solutions were prepared by dissolving 0·25525 and 0·5105 grm. potassium chromate in 1 litre of water made alkaline by a little sodium carbonate, each cubic centimetre then corresponding respectively to one-tenth and two-tenths m.grm. chromic oxide, in which latter form chromium is usually reported in rocks and ores. Definite amounts of one of the standards were then diluted with varying amounts of water in a tall square glass vessel with exactly parallel sides. Into an exact duplicate of this vessel 5 or more c.c. of the standard were introduced from a burette and diluted with water from another burette till exact agreement seemed to be reached on looking through the glasses horizontally.

In the accompanying tables are recorded all observations, without regard to the sequence in which they were made. No greater pains were taken to get exact agreement of colour than are ordinarily observed in our routine titanium estimations, which are carried out in a precisely similar manner, so that the results may be taken to represent every-day work without extreme precautions. In only two cases can the observations be considered really bad, viz., the third comparison of No. 6 and the first of No. 16.

The first table and the grand mean show an apparent personal tendency toward slightly high results, though it is possible that this is due to a slight difference in the internal dimensions of the two glasses, the same one always having been used for the standard solution. If this is so, a long series of tests with glasses reversed should give a general mean slightly below 100.

Testing the Method on Ores and Rocks.

In order to prove the value of the method in rock analysis, varying amounts of the standard solution were evaporated in a large crucible with 5 grms. of an iron ore carrying phosphorus and vanadium, and fused with 20 grms. of sodium carbonate and 3 grms. sodium nitrate. The aqueous extract, after reduction of manganese by methyl or ethyl alcohol, was nearly neutralised by nitric acid and evaporated to secure approximate separation of silica and alumina. As a precautionary measure, since a little chromium is usually carried down, the precipitate was ignited, silica was removed by hydrofluoric and sulphuric acids, the residue was fused with sodium carbonate, and alumina again separated as before. To the combined filtrate was added mercurous nitrate and the slightly washed copious precipitate of phosphate, chromate, vanadate, and carbonate of mercury was ignited with the paper in a platinum crucible, which can be done without much fear of loss or injury to the crucible. The residue was then fused with a little sodium carbonate, extracted with water, filtered into a graduated flask, and made up to 50 or 100 c.c., according to the intensity of the colour, and compared with the standard. A similar operation was carried out with a silicate rock. Table III. shows the results.

When the percentage of chromic oxide in an ore or mineral is more than about two-tenths per cent, and vanadium has not also to be estimated, much time may be spared by at once taking the colour of the original extract from the sodium carbonate fusion, after ensuring complete reduction and removal of manganese, and perhaps concentrating. But if the chromium is much less than this amount, and especially if several grms. of powder have been operated on, it becomes difficult or impossible to obtain a filtrate of sufficiently small bulk to show a decided colour. Therefore, in such cases, and when vanadium is likewise to be estimated, it is necessary to precipitate as above with mercurous nitrate in order to eventually have

* Read before the Washington Section, March 10, 1898. From the *Journal of the American Chemical Society*, xx., No 6, June, 1898.

TABLE I.

Ten c.c. standard represent one m.grm. chromic oxide.

No.	Test solution. Standard.	Test solution. Diluted with water.	Comparison standard.	H_2O added.	Contents, as chromic oxide.	Chromic oxide found.	Chromic oxide present.	Error.	Chromic oxide found.
	C.c.	C.c.	C.c.	C.c.	M.grms.	M.grms.	M.grms.	M.grm.	Per cent.
1.	10*	90*	5	44·00	0·5	0 98	1	−0·02	98·0
2.	20†	80†	5	21·00	0·5	1·92	2	−0·08	96·0
3.	40	60	10	14·60	1·0	4·06	4	+0·06	101·5
4.	40	60	9·7	14·25	0·97	4·05	4	+0·05	101·2
			10	13·95	1·0	4·17	4	+0·17	104·4
			10	14·30	1·0	4·11	4	+0·11	102·9
			10	14·20	1·0	4·13	4	+0·13	103·3
5.	40	60	10	14·65	1·0	4·05	4	+0·05	101·4
			10	15·65	1·0	3·90	4	−0·10	97·5
6.	40	60	10	15·25	1·0	3·96	4	−0·04	99·0
			10	14·30	1·0	4·11	4	+0·11	102·9
			10	13·15	1·0	4·32	4	+0·32	108·0
			10	14·75	1·0	4·04	4	+0·04	101·0
			20	29·50	2·0	4·04	4	+0·04	101·0
7.	50	50	10	9·75	1·0	5·06	5	+0·06	101·2
8.	50	50	10	10·00	1·0	5·00	5	0·00	100·0
9.	60	40	10	7·20	1·0	5·81	6	−0·19	96·7
10.	75	25	20	6·65	2·0	7·505	7·5	+0·005	100·1
			20	6·60	2·0	7·519	7·5	+0·019	100·2
			10	3·15	1·0	7·605	7·5	+0·105	101·4
			15	4·70	1·5	7·610	7·5	+0·11	101·5
11.	10	10	10	10·15	1·0	0·992	1	−0·008	99·2
			20	19·75	2·0	1·006	1	+0·006	100·6
12.	10	11	10	10·60	1·0	1·02	1	+0·02	102·0
13.	14·2	26·9	10	18·60	1·0	1·43	1·42	+0·01	100·7
			20	35·70	2·0	1·47	1·42	+0·05	103·5
14.	15	24·35	10	16·55	1·0	1·48	1·5	−0·02	98·7
15.	16	20	10	13·30	1·0	1·54	1·6	−0·06	96·2
			20	24·30	2·0	1·63	1·6	+0·03	101·9
16.	31·9	20·6	10·5	8·10	1·05	2·96	3·19	−0·23	92·8
			20·5	14·20	2·05	3·10	3·19	−0·09	97·2
17.	62·05	22·3	20	7·00	2·0	6·25	6·205	+0·45	100·7
			40	12·00	4·0	6·49	6·205	+0·285	104·6

Mean percentage found, 100·5.

* Colour in this dilution too faint.
† Limit of dilution for clear distinction of colour in a thickness of three and three-tenths c.m.

TABLE II.

Varying amounts of Standard No.2 (1 c.c. = 0·2 m.grm. Cr_2O_3) diluted till of the same concentration as Standard No. 1.

No.	Standard.	Water added.	Contents as chromic oxide.	Chromic oxide found per 100 c.c.	Chromic oxide present in 100 c.c.	Error.	Chromic oxide found.
	C.c.	C.c.	M.grms.	M.grms.	M.grms.	M.grm.	Per cent.
18.	5	5·2	1	9·80	10	−0·2	98·0
19.	10	9·95	2	10·02	10	+0·02	100·2
20.	15	15·8	3	9·74	10	−0·26	97·4
21.	20	20·0	4	10·00	10	0·00	100·0
22.	30	29·5	5	10·08	10	+0·08	100·8

Mean, 99·3. Grand mean, 100·36.

TABLE III.

		Chromic oxide added.	Chromic oxide found.
		M.grms.	M.grms.
I.	5 grms. iron ore	7·03	7·18
		—	7·20
		—	7·25
		—	7·21
II.	5 grms. iron ore	2·99	3·08
		—	3·13
III.	2 grms. silicate	1·6	1·53
		—	1·57
		—	1·59

a small bulk of sufficiently coloured solution. Even then, for very minute amounts, it is necessary to use Nessler tubes exactly as in ammonia estimations.

If nitre has been used in the fusion and the crucible has been attacked by it, a yellow colour of the filtrate may be due to dissolved platinum, but neither the proportion of nitre nor the temperature of the blast should ever be high enough to permit the crucible to be attacked.

(To be continued).

Agricultural Exhibition at Warsaw.—An Agricultural Exhibition will be held in the Museum of Trade and Agriculture, at Warsaw, from November 28th to December 5th, 1898.

THE TRANSITION TEMPERATURE OF SODIC SULPHATE, A NEW FIXED POINT IN THERMOMETRY.*

By THEODORE WILLIAM RICHARDS.

I. *On the Constancy of the Point in Question.*

With the assistance of Jessie Briggs Churchill.

According to the Phase Rule of Willard Gibbs, in order to obtain a nonvariant point in any system two more conditions must be definitely fixed than the number of components in the system. In other words, if the system contains only one component, three conditions must be fixed; if two components, four conditions, and so on. Since such a nonvariant† point is invariable in temperature, as well as in every other respect, there evidently exist a great number of definite temperatures obtainable by the combinations of different substances.

Of these multitudinous nonvariant points the world uses only two, the simplest possible, as the standards of thermometry. The fixed conditions are:—a definite pressure, and two phases of one component, water. While undoubtedly 0° and 100° C. will always remain the standards of reference, it would be extremely convenient to have at least one definitely determined point between these. Many thermometers do not cover this whole range, and all are noticeably upset as to their internal condition by such wide variations of temperature.

Landolt's very carefully made determinations of the melting-points of a number of organic substances (*Zeitsch. Phys. Chem.*, 1889, iv., 349) showed that these bodies are too much subject to contamination with clinging impurities to serve as accurate standards. Organic compounds are too plentiful in number to make the easy obtaining of any one alone an easy matter, and among inorganic substances no single suitable substance beside water seems to exist.

There is no reason, however, why we should be confined to the use of a single component in this search for fixed points. Two components, requiring four fixed conditions, should answer equally well. The only essential is that the substance involved should form perfectly definite phases, and should be capable of being obtained in the pure state. Nernst has suggested the use of "cryohydric" points as a means of maintaining constant low temperatures, but the possibility of utilising higher nonvariant points involving two components as a basis of thermometry and a means of maintaining constant temperature does not seem to have been generally realised.

Of the many pairs of substances which might serve the purpose in view, the pair, sodic sulphate and water, seems to be the most suitable for several reasons.

In the first place, the system ($Na_2SO_4 + Na_2SO_4.10H_2O$ + saturated solution + vapour) is in equilibrium at 32·5° (Lowenherz found 32·39°, *Zeitschr. Phys. Chem.*, xviii., 70)—a most convenient point, less above ordinary temperatures than 0° is below them, and within the field of even very large-bulbed thermometers. This small elevation involves very little disturbance in the tension of the glass, as well as very slight correction on account of the column projecting into the cooler atmosphere of the room. Moreover, 32·5° is near the temperature of greatest difference between the hydrogen and the mercury thermometer.

On the other hand, sodic sulphate does not "melt" so easily as to cause any difficulty in keeping it unfused in a reasonably warm place. A substance melting only a few degrees lower would be continually freezing into a solid lump, which could be extracted from its bottle only by melting. The fact that it is not deliquescent is also of value.

A much more important advantage, as far as exactness is concerned, is to be found in the great ease with which the substance may be obtained in a pure state. Its solubility is far less at 10° than it is at 33°—hence its recrystallisation by cooling does not involve much loss. Moreover, it may also be crystallised in the anhydrous state by simply melting the aqueous crystals; and since this process necessarily brings into play a wholly new set of isomorphous relations, it may be relied upon to eliminate impurites which are not rejected by the hydrated crystals.

Again, the "melting" absorbs enough heat to insure the rendering "latent" of any heat evolved by the mechanical process of gentle agitation, or of any heat taken in from the environment. The semi-opaque nature of the mixture removes any serious danger from radiant heat.

Since the volume scarcely changes with the transition, reasonable alterations in pressure do not cause any essential change in the temperature. This fact may be of importance if one has occasion to use very deep layers of the mixture.

The number of possible hydrates is smaller in this case than in many, hence the change is a sharp one. The salt $Na_2SO_4.7H_2O$ is so soluble that it cannot exist in the presence of the other solid phases.*

Last, but not least, Glauber's salt is extremely inexpensive, and at hand in every chemical and physical laboratory. Oddly enough, the melting-point of the anhydrous salt, 865°, is one of the most satisfactory standards among high nonvariant temperatures.

It is needless to state that the usual precautions necessary to obtain accurate results were taken in the thermometric work which follows, as well as in the chemical preparation. Several thermometers were used in the course of the experiments; they will be described as the account progresses. For the first determinations, which were wholly of a relative nature, a Beckmann thermometer of the first quality, made by Goetze, of Leipzig, was chosen. This instrument was graduated to hundredths of a degree, and could be easily read to within a thousandth. Because of the thinness of its bulb, this thermometer was especially sensitive to pressure; hence it was guarded carefully during its use. It was always read in a vertical position, as were all the other thermometers. Since the temperature of the room remained essentially constant during the preliminary experiments, the barometric pressure did not change by important amounts, and the height of the mixture around the bulb was always about the same, the readings are directly comparable with one another without correction.

First Problem.—The Effect of the Temperature of the Environment.

At first sodic sulphate prepared by crystallising twice in a porcelain dish the ordinary "purissimum" material of commerce was used. This preparation was coarsely powdered and partly dried in a desiccator. When placed in a wide test-tube surrounded by a Beckmann air-jacket (a still wider test-tube), and allowed to remain for an hour in a thermostat at 32·9°, it melted with absolute constancy at a temperature indicated on the arbitrary scale by 4·758. On the following day, upon being replaced in the thermostat the "melting" point appeared to be precisely the same. It was found advantageous to melt the crystals partially into a pasty mass, by means of a gas-lamp, before immersing them in the thermostat, and the mass was stirred

* From the *American Journal of Science*, vol. vi., 1898; also *Zeitschr. Phys. Chem.*, xxvi., 691.

† Trevor's term "nonvariant" is a peculiarly happy selection. His similar terms, "monovariant," &c., would be equally suitable if they were not hybrids of Greek and Latin. Would it not be well to use, instead of these, the homogeneous words "univariant," "bivariant," &c.? These latter terms are not likely to cause trouble because of their similarity to "univalent," &c., for both the numbers of syllables and the accents are different in the two series.

* The non-existence of the substance $Na_2SO_4.H_2O$ may now be considered proved. Even if it really exists, however, the facts recorded below remain: one must merely read "monohydrated" instead of "anhydrous," and the theory will be unchanged. See de Coppet, *Berichte d. D. Ch. Gesell.*, xii., 248; also, Lescœur, *Ann. Chim. Phys.*, 1890, [6], xxi., 526

gently by a ring-shaped platinum stirrer. Upon raising the temperature of the bath to 36° not the least change was observed, although this application of a higher temperature was allowed to continue for half an hour. A lower temperature, on the other hand, had a less satisfactory effect. When the bath was kept at 29° the thermometer in the sodic sulphate indicated a constant reading of 4·746, a depression of 0·012°. In order to verify this phenomenon, a purer specimen, which melted at 4·760° with the bath about 33°, was surrounded by an environment at 30°, and then indicated 4·750° on the arbitrary scale.

Thus it is evident that the most satisfactory results are to be obtained by melting the salt slowly, and not by allowing it to solidify. The reason for this is obvious. The anhydrous salt is far less apt to form supersaturated solutions than the hydrated salt, and the crystals instantly melt upon being heated above their transition point, absorbing an appreciable amount of heat in the process. On the other hand, in order that the mass may solidify, the anhydrous mass must dissolve while the supersaturated solution is depositing its hydrate, both of these operations being much less prompt than the preceding. In all subsequent determinations the thermostat was kept about half a degree above the point sought, and it was found that the mixture would then melt so slowly as to last for hours.

Second Problem.—Concerning the Purity of the Salt Required.

Löwenherz (*loc. cit.*) has found, under van 't Hoff's direction, that an admixture of foreign substances lowers the transition temperatnre of sodic sulphate just as it does simpler melting-points. Hence a study of the purification of the salt is of great importance for our present purpose.

The mother-substance used in preparing the salt above was found to melt at a temperature of 0·06° below that which had been twice re-crystallised in porcelain. Four further crystallisations in platinum vessels changed the transition temperature only 0·002 above that corresponding to two re-crystallisations, the arbitrary scale indicating 4·760°.

While it seemed probable that this re-crystallisation had freed the salt from anything which could affect its melting-point, further proof seemed proper. Hence a kilogrm. or so of pure sodic hydric carbonate was thoroughly washed with pure water, and was then dissolved in an excess of pure dilute sulphuric acid. After six crystallisations the salt was still perceptibly acid to methyl orange, and hence after testing the melting-point the salt was re-crystallised again, collected on a large Gooch crucible, and washed. Although now free from any trace of acid, it was precipitated as anhydrous salt by heating to 100° (the mother-liquor being rejected), re-dissolved at 33°, and re-crystallised by cooling. These final operations were conducted with the purest water and all the precautions necessary in the most refined work. A portion of the later mother-liquors was neutralised with pure soda and twice re-crystallised in order to obtain a third sample.

Another thermometer was used in testing the melting-points of these three samples. This thermometer, admirably made by Baudin of Paris, in 1880, is graduated to the fiftieth part of a degree, and can be read by means of a telescope and micrometer to within a thousandth. Its scale is about 40 c.m. long, and covering the twelve degrees between 21° and 33°, including the zero point below a small auxiliary bulb. This small bulb was always in the thermostat, leaving only about 10° of the column to be corrected for the lower temperature of the room. Following are the uncorrected results obtained with this thermometer;—

The slightly acid salt melted at	32·520
The neutralised and re-crystallised salt melted at	32·560
The purest, nine times re-crystallised salt melted at..	32·561
The twice re-crystallised salt first made melted at	32·560

The last observation was made in order to compare this series with the other which has been made with the Beckmann thermometer. As the pressure had increased since the other readings were taken, the arbitrary thermometer itself could not be satisfactorily compared with that of French manufacture.

Evidently it is a matter of no great difficulty to obtain sodic sulphate of constant "melting-point." Even two re-crystallisations of the purest Glauber's salt of commerce carried on in porcelain vessels seemed to be enough to eliminate any serious impurity. In order to obtain certain results, the purification should be continued until the melting-point is constant. The repeated re-crystallisation of the slightly acidified salt is especially instructive in this regard, for it is safe to conclude that when the acid has gone other accidental impurities would have disappeared also; and the methyl-orange test is one of extreme delicacy if the solution is not too concentrated.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 28th, 1898.

Mr. Shelford Bidwell, President, in the Chair.

A paper was read by Mr. W. R. Pidgeon, on "*An Influence Machine.*"

The machine, which was exhibited, consists of a pair of glass discs, rotating in opposite directions upon a spindle. They are partially covered on one face with narrow radial sectors of tin-foil, each provided with a small brass knob. This face of the disc, including its sectors, is then coated with insulating wax, leaving only the knobs projecting through the wax. Two earthing-brushes pass through two insulated fixed inductors, and support them. The inductors are kept charged by exploring-points connected to each, and placed so as to collect electricity from the revolving discs. By means of brushes, the sectors on each of the discs are successively earthed at the moment they pass the fixed inductors, *i. e.*, at the moment that their capacity is a maximum; and they are made to deliver up their charge to the main collecting brushes at the moment when they are electrically farthest from the inductors, *i. e.*, when their capacity is a minimum. Hence, if there is no loss of electricity in the process, the potential at the collecting brushes is proportionally high. Each sector of a particular disc, as it moves away from its inductor with rising potential, induces a corresponding potential on the sectors opposed to it on the second disc; this action is cumulative. The thick coating of wax restricts leakage to the small area of the contact knobs, so that surface effects of dirt and moisture are minimised.

Capt. J. H. Thomson, R.A., said that, apart from its electrical merits, the machine possessed advantages in mechanical construction. He thought there was still room for improvement in this respect. The counter-shaft should be done away with, and ball-bearings should be introduced. The inductor was a distinct improvement;

he thought the efficiency might be increased by adding other inductors. Platinum-iridium was the best material for brushes of such machines.

Prof. Ayrton asked what efficiency was obtained with modern influence machines in general.

Capt. Thomson had found that when running a machine by a motor, about 80 per cent of the power was wasted in mechanical friction; of the remaining 20 per cent a great deal was lost as electrical leakage.

Prof. S. P. Thompson thought it had been pointed out by Mr. Wimshurst that influence machines did not work well unless there were at least two thicknesses of glass between the inducing and induced conductors. That was why Mr. Wimshurst put his sectors on the outer faces of the glass discs. Mr. Pidgeon had departed from this. The advantage of the narrow spacing of the sectors was not very apparent.

Mr. Wimshurst (abstract of communication). Waxing the discs reduces leakage and increases the output; the wax-coating virtually doubles the number of plates. Inductors contribute a further increase to the output. In 1883 Mr. Wimshurst tried thick coatings of shellac, and also, duplicating the glass, with in some cases sectors upon the second glass to increase the capacity. The output was increased, but the construction lost simplicity. The indifference of Mr. Pidgeon's machine to dirt and dust was a most valuable result.

Mr. Pidgeon, in reply, showed a set of secondary inductors such as Capt. Thomson had just proposed. They improved the output by about 15 per cent, but they were troublesome to keep in order, for they increased the tendency to "reverse."

Dr. S. P. Thompson then repeated an experiment, discovered by Prof. Righi, on "*A Magneto-optic Phenomenon.*" It was originally described in *Roma, R. Accad. Lincei*, Atti. 7, Ser. 5, 1898.

A substance absorptive of light is submitted to a powerful magnetic field between the pole-pieces of an electro-magnet. The pole-pieces are drilled so that a beam of light from an arc-lamp can traverse the gap *along* the magnetic lines. A polarising prism is placed between the arc-lamp and the electro-magnet. After having passed through the magnetising apparatus, the beam thus polarised is examined by an analyser. The analyser must be turned to "extinction" before the magnetising current is turned on. If this is done, brightness is restored at the analyser as soon as the magnetic field is established. The substance absorbing the light in the gap may be nitric oxide fumes, or an ordinary spirit-lamp sodium flame. The second effect to be noticed is that when the emergent beam is examined there is a splitting of the lines. Righi explains this by supposing that when light of frequency, n, is brought into a magnetic field and passed *along* the lines of the field, it is split up into two sets of circular waves, a right-handed and a left-handed set, one of which sets is accelerated and the other retarded. There are now two frequencies, n_1, n_2, one a little higher and the other a little lower than n. But since the analyser is adjusted to extinguish n, there is brightness for n_1, n_2. Normally, nitric oxide absorbs green, and red is observed; but when the magnetic field is set up, blue-green light is seen at the analyser; for there are now two different kinds of light being absorbed, one of higher and one of lower frequency than the normal, and what is observed is the complementary spectrum. Again, if a tube of sodium is warmed to a point far short of that which would cause it to emit visible rays, and the vapour is passed into the magnet gap, at the moment when the magnetic field is set up the D line becomes visible in the observing spectroscope, *i. e.*, the emission spectrum is obtained of a substance which is not actually emitting light.

Mr. Blakesley said that no doubt the analyser was used at the position of extinction for convenience merely. In other positions the eye would be overwhelmed with light.

Mr. Albert Campbell then read a paper on "*The Magnetic Fluxes in Meters and other Electrical Instruments.*"

He has recently undertaken the measurement of the magnetic fluxes and fields in certain instruments, to determine the order of magnitude of the flux density. In other cases the *total* flux is measured; and in the tests on meters the power lost in the various parts of the instruments is determined. For the measurement of B the ordinary ballistic-galvanometer method is employed, with an exploring-coil. But for alternating fluxes two special methods are adopted, in the first of which the exploring-coil is in series with a heating-coil associated with a thermopile; in the second, a telephone is connected in series with the search-coil and a potentiometer resistance strip. A constant current is sent through the strip from the main alternate-current circuit supplying the meter or other apparatus; the telephone and search-coil therefore form a shunt to that circuit at the strip. The search-coil is put into position in the field to be tested, and the strip is then adjusted to give silence in the telephone. All these methods are described in detail in the paper, and very important deductions are made, especially as regards the influence of the earth's field on instruments generally assumed to be independent of the earth's H. In a few cases diagrams are given of the fluxes in magnets, showing exactly what proportion of the total flux is effective at the gap.

Dr. S. P. Thompson suggested that, as the paper was of great significance to all who were interested in the design of electric meters and other measuring instruments involving a knowledge of magnetic fluxes and their variation, an opportunity should be given for a full discussion.

The President proposed votes of thanks, and adjourned the discussion of Mr. Campbell's paper to the next meeting, on Nov. 11th.

NOTICES OF BOOKS.

An Introduction to the Science and Practice of Qualitative Chemical Analysis, Inorganic. By Chapman Jones, F.I.C., F.C.S. London: Macmillan and Co., Ltd.

This volume is one more addition to the already long list of text-books for Science students, and is the outcome of the author's experience as a demonstrator and examiner in Chemistry: it will doubtless be of great assistance to students attending Science classes. The methods of analysis are clearly stated, and great pains have been taken to give precise direction in every detail.

The object of the author has been to thoroughly ground the student in sound method in his work; but we are unable to avoid the impression that there is a danger of his trusting to his text-book rather than to his memory.

An original feature is the printing of the included tables of Analysis upon parchmentised paper, "so that if anything is spilled on the book as it lies open at any of the tables the result will not be so disastrous as it otherwise might be." This appears an unfortunate way of meeting a well-known difficulty with the average student, and seems to suggest working with a test-tube in one hand and the text-book in the other, a system to be deprecated.

In the table of atomic weights two values are given, one said to be deduced from the most reliable experimental data available (praseo- and neo-dymium are not included), and the second "sufficiently near for all the calculations for which the student may require atomic weights: thus the atomic weight of chlorine is given in the first column as 35·453, and in the second as 35·5. Surely it would have been better to have credited the student with a certain amount of reasoning power, and have left him to deduce this for himself.

A Pocket Dictionary of Hygiene. By C. T. KINGZETT, F.I.C., and D. HOMFRAY, B.Sc. London: Baillière, Tindall, & Cox, 20 & 21, King William Street, Strand.

AN exceedingly useful little book, full of commonplace, but valuable, information. Although professedly the chief object of the authors has been to produce a concise dictionary for the use of medical and sanitary officers, it would undoubtedly prove of great service not only to those professionally interested in hygiene, but also to any one having household responsibilities.

The brief tables on the effects of vaccination would be a good lesson to the so-called "conscientious objector," could he be persuaded to read anything so matter-of-fact.

We must say we were surprised on finding an article on Röntgen rays, embracing Crookes's, Hertz's, and Röntgen's researches; but hygiene is a very inclusive subject.

The book is very well printed and conveniently arranged in alphabetical order, and not too large to be easily carried in the pocket.

The Cyanide Process for the Extraction of Gold, and its Application on the Witwatersrand Goldfields and Elsewhere. By M. EISSLER. Second Edition, Enlarged. London: Crosby Lockwood and Son, 7, Stationers' Hall Court, Ludgate Hill.

THE second edition of this valuable work will be welcomed by all interested in gold extraction; its thoroughly practical character renders it of the greatest value to metallurgists, especially those actively engaged in gold recovery

Mr. Eissler has spared no pains in his exposition of the process; it is clearly written, and there are plenty of illustrations as well as some fifteen folding plates giving detailed plans of the plants erected in various localities.

A good description is included of the Siemens-Halske process for the precipitation of gold from cyanide solutions, and an Appendix giving an up-to-date account of the cyanide plant recently erected at Golden Gate Mill, at the De la Mar Company, at Merceer, Utah, U.S.A.

A Short Manual of Analytical Chemistry, Qualitative and Quantitative, Inorganic and Organic, following the Course of Instruction given in the Laboratories of the South London School of Pharmacy. By JOHN MUTER, Ph.D., F.R.S.E., F.I.C., F.C.S. Eighth Edition, Illustrated. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd.

THE fact that this work has reached its eighth edition speaks eloquently as to its general appreciation, and the author is to be congratulated upon his success, due undoubtedly to the thoroughly practical manner in which the subject is handled: certainly it is not a "mere examination book," and the pharmaceutical student who makes good use of it cannot fail to acquire a solid grounding in the science. There are plenty of illustrations, particularly in the chapters upon manipulation, which are of very great value to the beginner, as they show, far more clearly than the most elaborate description, the proper way to conduct simple operations.

From a pharmaceutical point of view, the fact that this edition contains the present legal standards for drugs as fixed by the B.P. makes it valuable as a book of reference. It is well and clearly printed, and the price is so low as to place it within the reach of all.

Inorganic Chemistry, according to the Periodic Law. By F. P. VENABLE and JAS. LEWIS HOWE. Easton, Pennsylvania: The Chemical Publishing Co. 1898. Pp. vi.—266. 8vo. Illustrated.

"THE Periodic Law has come to be the great central fact of chemistry; it has thrown new light upon the study of the science and is the very best aid to that study." This statement, enunciated in the Preface, forms the underlying principle throughout this book, thus securing thorough systematic instruction with economy of time. Scattered through the work are directions for simple experiments that have been found by experience well calculated to impress the subject upon the student. One hour of laboratory work is recommended in connection with each lecture. In Part I. the great principles of the science are laid down in an excellently clear style, developing especially the Periodic Law. The authors anticipate, however, the difficulties students encounter in attempting to comprehend the theories of chemistry, and therefore a good deal of the matter is repeated in suitable places when facts have been acquired which render explanations possible. At the same time it is scarcely practicable to start upon the study of the science without some such framework for the building.

The important facts of elementary chemistry are given with conciseness and clearness, the order in Part II. being H, Fl, Br, I, followed by O, S, Se, Te, N (atmosphere), P, As, Sb, and Bi. The space given to the several elements is proportioned to their relative importance with great nicety, and much economy of space is gained by treating together groups of analogous compounds.

After dealing with the elements, the authors introduce the student to hydrides, halides, oxides and sulphides, and other binary compounds. This arrangement is strictly logical, but it has the disadvantage of postponing the student's full acquaintance with such common substances as nitric and sulphuric acid until towards the close of the volume, although he has been using these acids in experimental work from the beginning.

The spelling recommended by the American Association for the Advancement of Science has been adopted only in part, the authors not venturing to write "sulfur" for the customary "sulphur," which was never justified etymologically.

Professor F. B. Venable, Ph.D., of the University of North Carolina, is well known as the author of "The Development of the Periodic Law" (1896), "A Short History of Chemistry" (1894), and many original investigations. Professor Jas. Lewis Howe, M.D., Ph.D., has recently published, through the Smithsonian Institution, an invaluable Bibliography of Platinum and associated metals. These two chemists have produced a book of great merit, being fully up to date (even krypton, neon, and metargon are briefly noticed), and well adapted for instruction.

The volume is well printed, but the paper seems unnecessarily bulky. There is an index. The buckram binding is serviceable. H. C. B.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Royal Institution, 5. General Monthly Meeting.
FRIDAY, 11th.—Physical, 5. Discussion on Mr. Campbell's Paper on "The Magnetic Fluxes in Meters and other Electrical Instruments," to be opened by Prof. W. E. Ayrton, F.R.S. "Propagation of Damped Electrical Oscillations along Parallel Wires," by Prof. W. B. Morton, M.A. "Properties of Liquid Mixtures," by R. A. Lehfeldt.

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London: EDWARD STANFORD, 26 and 27, Cockspur Street, Charing Cross, S.W.

THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2033.

THE CHEMISTRY OF THE STARS.*

By Sir J. NORMAN LOCKYER, K.C.B., F.R.S.

The importance of practical work, the educational value of the seeking after truth by experiment and observation on the part of even young students, are now generally recognised. That battle has been fought and won. But there is a tendency in the official direction of seats of learning to consider what is known to be useful, because it is used, in the first place. The fact that the unknown—that is, the unstudied—is the mine from which all scientific knowledge with its million applications has been won is too often forgotten.

Bacon, who was the first to point out the importance of experiment in the physical sciences, and who predicted the applications to which I have referred, warns us that "lucifera experimenta non fructifera quaerenda"; and surely we should highly prize those results which enlarge the domain of human thought and help us to understand the mechanism of the wonderful universe in which our lot is cast, as well as those which add to the comfort and the convenience of our lives.

It would be also easy to show by many instances how researches, considered ideally useless at the time they were made, have been the origin of the most tremendous applications. One instance suffices, Faraday's trifling with wires and magnets has already landed us in one of the greatest revolutions which civilisation has witnessed; and where the triumphs of electrical science will stop no man can say.

Fraünhofer at the beginning of this century examined sunlight and starlight through a prism. He found that the light received from the sun differed from that of the stars. So useless did his work appear that we had to wait for half a century till any considerable advance was made. It was found at last that the strange "lines" seen and named by Fraünhofer were precious indications of the chemical substances present in worlds immeasurably remote. We had, after half a century's neglect, the foundation of solar and stellar chemistry, an advance in knowledge equalling any other in its importance.

The first important matter which lies on the surface of such a general inquiry as this is that if we deal with the chemical elements as judged by the lines in their spectra, we know of the existence of oxygen, of nitrogen, of argon, representing one class of gases, in no celestial body whatever; whereas, representing other gases, we have a tremendous demonstration of the existence of hydrogen and helium.

We see, then, that the celestial sorting out of gases is quite different from the terrestrial one.

Among the non-metals there is a considerable development of carbon in some stars, and an indication of silicium in others, while among the metals are found chiefly Ca, Sr, Fe, Mg.

These elements do not exist indiscriminately in all celestial bodies.

From a spectroscopic study of those stars which resemble our sun, we learn that the atmospheres of some consist chiefly of those elements known to us as gaseous, of others chiefly metallic, and of others, again, carbon or compounds of carbon. This is evidence of variation in the chemical constitution of stellar atmospheres; also, as one of Kirchhoff's laws shows, that the hotter a mass of matter is, the further its spectrum extends into the ultra-violet. Hence, the hotter a star is, the further its complete or continuous spectrum will extend towards the ultra-violet.

Now to deal with three of the main groups of stars, we find the following very general result:—

Gaseous stars	Longest spectrum.
Metallic stars	Medium spectrum.
Carbon stars	Shortest spectrum.

Therefore—

Gaseous stars	Highest temperature.
Metallic stars	Medium temperature.
Carbon stars	Lowest temperature.

Hence the differences in apparent chemical constitutions are associated with differences of temperature.

Research also shows that, in the case of Mg, Fe, Ca, &c., by increasing the temperature in which they are volatilised, new lines are added or old ones intensified; applying this to stellar spectroscopy, it is found that—

Gaseous stars..Highest temperature	Strong helium and faint enhanced lines.
Metallic stars..Medium temperature	Feeble helium and strong enhanced lines.
	No helium and strong arc lines.
Carbon stars ..Lowest temperature	Faint arc lines.

It is clear now, not only that the spectral changes in stars are associated with, or produced by, changes of temperature, but that the study of the enhanced spark and the arc lines lands us in the possibility of a rigorous stellar thermometry, such lines being more easy to observe than the relative lengths of spectrum.

Many years of very detailed inquiry have convinced me that all stars save the hottest must be sorted out into two series—those getting hotter, and those, like our sun, getting cooler—and that the hottest stage in the history of a star is reached near the middle of its life.

The method of inquiry adopted has been to compare large-scale photographs of the spectra of the different stars, taken by my assistants at South Kensington; the complete harmony of the results obtained along various lines of other work carries conviction with it.

We find ourselves, then, in the presence of minute details exhibiting the workings of a chemical law, associated distinctly with temperature.

What, then, is the chemical law? It is this. In the very hottest stars we deal with the gases hydrogen, helium, and doubtless others still unknown, almost exclusively. At the next lowest temperatures we find these gases being replaced by metals in the state in which they are observed in our laboratories when the most powerful jar-spark is employed. At a lower temperature still, the gases almost disappear entirely, and the metals exist in the state produced by the electric arc. Certain typical stars showing these chemical changes may be arranged as follows:—

Stars getting hotter.	Hottest stars.	Stars cooling.
	Bellatrix	
	ζ Tauri	β Persei
Rigel		γ Lyra
α Cygni		Castor
γ Cygni		Procyon
α Orionis		Arcturus and Sun

We get a great diversity, and we know that this diversity accompanies changes of temperature. We have also found that the sun, which we independently know to be a cooling star, and Arcturus, are identical chemically.

The next point we have to consider is whether the

* Abstract of the Presidential Address to the Birmingham and Midland Institute, October 26, 1898.

absorption which the spectrum indicates for us takes place from top to bottom of the atmosphere, or only in certain levels.

In many of these stars the atmosphere may be millions of miles high. In each the chemical substances in the hottest and coldest portions *may* be vastly different; the region, therefore, in which this absorption takes place, which spectroscopically enables us to discriminate star from star, must be accurately known before we can obtain the greatest amount of information from our inquiries.

Our next duty then clearly is to study the sun—a star so near us that we can examine the *different parts* of its atmosphere, which we cannot do in the case of the more distant stars. By doing this we may secure facts which will enable us to ascertain in what parts of the atmosphere the absorption took place which produces the various phenomena on which the chemical classification has been based.

It is obvious that the general spectrum of the sun, like that of stars generally, is built up of all the absorptions *which can make themselves felt* in every layer of its atmosphere from bottom to top, that is from the photosphere to the outermost part of the corona. Let me remind you that this spectrum is *changeless* from year to year.

Now sun-spots are disturbances produced in the photosphere; and the chromosphere, with its disturbances, called prominences, lies directly above it. Here, then, we are dealing with the lowest part of the sun's atmosphere. We find first of all that in opposition to the changeless general spectrum, great changes occur with the sun-spot period, both in the spots and chromosphere.

The spot spectrum is indicated, as was found in 1866, by the widening of certain lines; the chromospheric spectrum, as was found in 1868, by the appearance at the sun's limb of certain bright lines. In both cases the lines affected seen at any one time are relatively few in number.

In the spot spectrum, at a sun-spot minimum, we find iron lines chiefly affected; at a maximum they are chiefly of unknown or unfamiliar origin. At the present moment the affected lines are those recorded in the spectra of vanadium and scandium, with others never seen in a laboratory. That we are here far away from terrestrial chemical conditions is evidenced by the fact that there is not a gramme of scandium available for laboratory use in the world at the present time.

Then we have the spectrum of the prominences and the chromosphere. That spectrum we are enabled to observe every day when the sun shines, as conveniently as we can observe that of sun-spots. The chromosphere is full of marvels. At first, when our knowledge of spectra was very much more restricted than now, almost all the lines observed were unknown. In 1868 I saw a line in the yellow which I found behaved very much like hydrogen, though I could prove that it was not due to hydrogen; for laboratory use the substance which gave rise to it I called helium. Next year I saw a line in the green at 1474 of Kirchhoff's scale. That was an unknown line, but in some subsequent researches I traced it to iron. From that day to this we have observed a large number of lines. They have gradually been dragged out from the region of the unknown, and many are now recognised as enhanced lines, to which I have already called attention as appearing in the spectra of metals at a very high temperature. The best time for observation is undoubtedly during an eclipse.

A tremendous flood of light has been thrown upon it by the use of large instruments constructed on a plan devised by Respighi and myself in 1871. These give us an image of the chromosphere painted in each one of its radiations, so that the exact locus of each chemical layer is revealed. One of the instruments employed during the Indian eclipse of this year is that used in photographing the spectra of stars, so that it is now easy to place photographs of the spectra of the chromosphere obtained during a total eclipse and of the various stars side by side.

Studying the spectra photographed during the eclipse of this year we see that practically the lower part of the sun's atmosphere, if present by itself, would give us the lines which specialise the spectra of γ Cygni or Procyon.

I recognise in this result a veritable Rosetta stone which will enable us to read the celestial hieroglyphics presented to us in stellar spectra, and help us to study the spectra and to get at results much more distinctly and certainly than ever before.

One of the most important conclusions we draw from the Indian eclipse is that, *for some reason or other*, the lowest hottest part of the sun's atmosphere does not write its record among the lines which build up the general spectrum so effectively as does a higher one.

There was another point especially important on which we hoped for information, and that was this:—Up to the employment of the prismatic camera insufficient attention had been directed to the fact that in observations made by an ordinary spectroscope, no true measure of the height to which the vapours or gases extended above the sun could be obtained; early observations, in fact, showed the existence of glare between the observer and the dark moon; hence it must exist between us and the sun's surroundings.

The prismatic camera gets rid of the effects of this glare, and its results indicate that the effective absorbing layer—that, namely, which gives rise to the Fraünhofer lines—is much more restricted in thickness than was to be gathered from the early observations.

It happened that I was the only person that saw both the eclipse of 1871 at the maximum of the sun-spot period and that of 1878 at minimum: the corona of 1871 was as distinct from the corona of 1878 as anything could be. In 1871 we got nothing but bright lines indicating the presence of gases, namely, hydrogen and another, since provisionally called coronium. In 1878 we got no bright lines at all, so I stated that probably the changes in the chemistry and appearance of the corona would be found to be dependent upon the sun-spot period, and recent work has borne out that suggestion.

General Results regarding the Locus of Absorption in Stellar Atmospheres.

We learn from the sun, then, that the absorption which defines the spectrum of a star is the absorption of a middle region, one shielded both from the highest temperature of the lowest reaches of the atmosphere where most tremendous changes are continually going on, and the external region where the temperature must be low, and where the metallic vapours must condense.

So far I have only dealt in detail with the hotter stars, but I have pointed out that we have two distinct kinds of coolest ones, the evidence of their much lower temperature being the shortness of their spectra. In one of these groups we deal with absorption alone, as in those already considered; we find an important break in the phenomena observed; helium, hydrogen, and metals have practically disappeared, and we deal with carbon absorption alone.

But the other group of coolest stars presents us with quite new phenomena. We no longer deal with absorption alone, but accompanying it we have radiation, so that the spectra contain both dark lines and bright ones. Now since such spectra are visible in the case of new stars, the ephemera of the skies, which may be said to exist only for an instant relatively, and when the disturbance which gives rise to their sudden appearance has ceased, we find their places occupied by nebulæ, we cannot be dealing here with stars like the sun, which has already taken some millions of years to slowly cool, and requires more millions to complete the process into invisibility.

The bright lines seen in the large number of permanent stars which resemble these fleeting ones—*new stars*, as they are called—are those discerned in the once mysterious

nebulæ which, so far from being stars, were supposed not many years ago to represent a special order of created things.

Now the nebulæ differ from stars generally in the fact that in their spectra we have practically to deal with radiation alone; we study them by their bright lines, the conditions which produce the absorption by which we study the chemistry of the hottest stars are absent.

A New View of Nebulæ.

Passing over the old views, among them one that the nebulæ were holes in something dark which enabled us to see something bright beyond, and another that they were composed of a fiery fluid, I may say that not long ago they were supposed to be masses of gases only, existing at a very high temperature.

Now, since gases may glow at a low temperature as well as at a high one, the temperature evidence must depend upon the presence of cool metallic lines and the absence of the enhanced ones.

The nebulæ, then, are relatively cool collections of some of the permanent gases and of some cool metallic vapours, and both gases and metals are precisely those I have referred to as writing their records most visibly in stellar atmospheres.

Now can we get more information concerning this association of certain gases and metals? In laboratory work it is abundantly recognised that all meteorites (and many minerals) when slightly heated give out permanent gases, and under certain conditions the spectrum of the nebulæ may in this way be closely approximated to. I have not time to labour this point, but I may say that a discussion of all the available observations to my mind demonstrates the truth of the suggestion, made many years ago by Prof. Tait before any spectroscopic facts were available, that the nebulæ are masses of meteorites rendered hot by collisions.

Surely human knowledge is all the richer for this indication of the connection between the nebulæ, hitherto the most mysterious bodies in the skies, and the "stones that fall from heaven."

Celestial Evolution.

But this is, after all, only a stepping-stone, important though it be. It leads us to a vast generalisation. If the nebulæ are thus composed, they are bound to condense to centres however vast their initial proportions, however irregular the first distribution of the cosmic clouds which compose them; each pair of meteorites in collision puts us in mental possession of what the final stage must be. We begin with a feeble absorption of metallic vapours round each meteorite in collision; the space between the meteorites is filled with the permanent gases driven out further afield and having no power to condense. Hence dark metallic and bright gas lines. As time goes on the former must predominate, for the whole swarm of meteorites will then form a gaseous sphere with a strongly heated centre, the light of which will be absorbed by the exterior vapour.

The temperature-order of the group of stars with bright lines as well as dark ones in their spectra, has been traced, and typical stars indicating the chemical changes have been as carefully studied as those in which absorption phenomena are visible alone, so that now there are no breaks in the line connecting the nebulæ with the stars on the verge of extinction.

Here we are brought to another tremendous outcome, that of the evolution of all cosmical bodies from meteorites, the various stages recorded by the spectra being brought about by the various conditions which follow from the conditions.

These are, shortly, that at first collisions produce luminosity among the colliding particles of the swarm, and the permanent gases are given off and fill the interspaces. As condensation goes on, the temperature at the centre of condensation always increasing, all the meteorites in time are driven into a state of gas. The meteoritic bombardment practically now ceases for lack of material, and the future history of the mass of gas is that of a cooling body, the violent motions in the atmosphere while condensation was going on now being replaced by a relative calm.

The absorption phenomena in stellar spectra are not identical at the same mean temperature on the ascending and descending sides of the curve, on account of the tremendous difference in the physical conditions.

In a condensing swarm, the centre of which is undergoing meteoritic bombardment from all sides, there cannot be the equivalent of the solar chromosphere; the whole mass is made up of heterogeneous vapour at different temperatures, and moving with different velocities in different regions.

In a condensed swarm, of which we can take the sun as a type, all action produced from without has practically ceased; we get relatively a quiet atmosphere and an orderly assortment of the vapours from top to bottom, disturbed only by the fall of condensed metallic vapours. But still, on the view that the differences in the spectra of the heavenly bodies chiefly represent differences in degree of condensation and temperature, there can be, *au fond*, no great chemical difference between bodies of increasing and bodies of decreasing temperature. Hence we find, at equal mean temperatures on opposite sides of the temperature curve, this chemical similarity of the absorbing vapours proved by many points of resemblance in the spectra, especially the identical behaviour of the enhanced metallic and cleveite lines.

A quarter of a century ago I pointed out that all the facts then available suggested the hypothesis that in the atmospheres of the sun and stars various degrees of "celestial dissociation" were at work, a "dissociation" which prevented the coming together of the finest particles of matter which at the temperature of the earth, and at all artificial temperatures yet attained here, compose the metals, the metalloids, and compounds.

On this hypothesis the so-called atoms of the chemist represent not the origins of things, but only early stages of the evolutionary process.

At the present time we have tens of thousands of facts which were not available twenty-five years ago. All these go to the support of the hypothesis, and among them I must indicate the results obtained at the last eclipse, dealing with the atmosphere of the sun in relation to that of the various stars of higher temperature to which I called your attention. In this way we can easily explain the enhanced lines of iron existing practically alone in Alpha Cygni. I have yet to learn any other explanation.

AMORPHOUS SILICA.

By ROBERT MELDRUM, F.C.S.

This investigation was originally carried out with the view of making a complete chemical and physical examination of amorphous silica, but after being in progress for some time it had to be abandoned through the pressure of other work. The following is a record of the results so far obtained:—

A sample of SiO_2 was prepared by adding 200 c.c. strong HCl to 200 c.c. of commercial sodium silicate, of sp. gr. 1·526, containing 12·87 per cent Na_2O and 31·98 per cent SiO_2. The mass was constantly stirred for thirty minutes, so as to allow the acid to thoroughly penetrate the thick gelatinous mixture, the yellow liquid decanted, and the SiO_2 washed repeatedly with boiling water until free from chlorine. After drying slowly in the air for a week, the resulting product was a snow-white, granular, coarse powder, very porous and light. Three determinations of the loss on ignition, at red heat, gave 30·4, 30·5, 30·35 —average 30·41 per cent. After drying over sulphuric

acid, until weight remained constant, lost 22·90 per cent, = 9·74 per cent H_2O in desiccated SiO_2. The specific gravity of the anhydrous silica was found to be 1·990, 2·0964; of the air-dry, 2·0543. Loss of air-dry at 100° C. = 24·75 per cent = 7·52 per cent H_2O in residue. When strongly ignited for thirty minutes over blowpipe, digested in water for twenty-four hours, allowed to dry in air until weight remained constant, absorbed parts per 100, 4·05, 4·65. Another portion of the strongly ignited sample, exposed to a moist atmosphere, absorbed 6·85 parts per 100.

Another sample was prepared, exactly as described above, but using a weaker solution of silicate, and dilute acid (equal parts strong HCl and water). Sp. gr. of air-dry 1·709, 1·7346. Its shrinkage was ascertained by filling a very strong-stoppered bottle of 8 c.c. capacity, and beating the bottom with a small mallet, adding more material and repeating this until the level ceased to diminish, the SiO_2 being previously passed through a 40-sieve. The bottle held 5·01, 5·08, and 5·00 grms.; thus showing that measuring powders by this method is fairly accurate. After ignition these were found to occupy volumes of 5·2 cc., 5·5 c.c., and 5·0 c.c., equal to 65, 68, and 62·5 per cent of original volume. The shrinkage is, therefore, much greater than the loss by weight on ignition, the latter being 25·80 per cent. Loss at 100° C. = 19·15, 19·35 per cent = 8·11 per cent H_2O in residue.

The following experiment was made to ascertain to what extent the density of SiO_2 would be increased when liberated from a strong solution of silicate, and in the presence of as little water as possible. For this purpose strong H_2SO_4 was poured very gradually into the silicate, well agitating and mixing the mass, so as to allow thorough decomposition. It was then allowed to digest for an hour, water added, and the amorphous silica partially washed by decantation, boiled with dilute HCl, and repeatedly boiled with distilled water till free from chloride. The variety obtained by this process is more granular, hard, and brittle, but less opaque, than the others. After strong ignition at red heat its specific gravity was found to be 2·008, 2·006. Lost over H_2SO_4, 23·55 per cent = 9·83 per cent H_2O in residue. Loss at red heat, 23·55 per cent. No increase of temperature was observed on moistening the anhydrous SiO_2 with water.

Of the various degrees of hydration obtained as noted above, the only ones approaching a definite hydrate are those resulting from the dehydration of the air-dry silica over H_2SO_4, which agree closely with the formula $3SiO_2.H_2O$. This confirms Merz's observation that the same hydrate is formed by prolonged drying of precipitated SiO_2 over H_2SO_4.

NOTE. — The samples were washed until free from gelatinous silica.

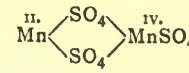
THE

FORMATION OF ALUMS BY ELECTROLYSIS.*

By JAS. LEWIS HOWE and E. A. O'NEAL.

THE work herein described had for its special end the formation of alums of manganese; and while, in this particular, success was not attained, it is felt that it is well to place the work on record, especially as phases of it are capable of further development, from which interesting results may be hoped.

Manganese salts in which the metal is trivalent, are not very satisfactorily known. Potassium and ammonium manganic alums have been described by Mitscherlich, but to manganic sulphate, $Mn_2(SO_4)_3$, Franke (*Journ. Prakt. Chem.*, [2], xxxvi., 451), who has most thoroughly studied it, gives the formula—



A salt of this constitution could hardly give an alum, and the literature of the manganese alums is very unsatisfactory. It was hoped by using the oxidising action of the electric current on a solution of manganous sulphate in the presence of an alkaline sulphate, manganic alum might crystallise out, and the reaction was studied with other metals for the sake of familiarity with the method and for comparison. Incidentally several alums were obtained and analysed which have not been previously described.

a. Iron Alums.— Apparatus:—Positive electrode, a platinum dish of about 250 c.c. capacity resting on a coil of heavy copper wire; negative electrode, a coil of heavy platinum wire; diaphragm, the lower portion of the porous cup of a Bunsen cell. In different experiments different batteries were used, but Bunsen or crowfoot cells were generally used.

The following is a specimen experiment:—Inner solution, ferrous sulphate strongly acidified with sulphuric acid; outer solution, saturated with ferrous sulphate and ammonium sulphate, and also strongly acidified with sulphuric acid; six crowfoot cells; current, 0·04 ampère. In forty-eight hours a large crop of beautiful iron-ammonium alum crystals, of perfect octahedral form, were produced. In one experiment, with solutions as above and apparatus also, except that Bunsen cells were used, with current 0·02 ampères, 41 grms. of iron-ammonium alum were obtained in twenty-four hours. This method is probably applicable to the formation of this alum on a commercial scale, having as its advantages the ease with which it is conducted and the fine quality of the product. Owing to the lesser solubility of potassium sulphate, the method, while successful, does not give such good results in the formation of iron-potassium alum.

The formation of iron-sodium alum was tried, using solutions as above, with sodium sulphate substituted for ammonium sulphate. Current, four Bunsen cells. After twelve hours the outer solution (+) was pink, and in twenty-four hours had become dark purple, resembling almost a solution of potassium permanganate, while oxygen bubbles were given off at the positive pole. A little ferrous sulphate solution was added, at which the colour at once disappeared, but after several hours with the current, it again became dark purple. The colour disappeared at once with reducing agents. The colour was that of ferrates, but the presence of ferric acid is hardly probable, and the solution being strongly acid, ferrates could not be present. It seems more probable that the compound was one of persulphuric acid. No crystals could be obtained even by using a freezing mixture. Some of the solution set aside for several weeks left, on evaporation, a hard, dirty violet, crystalline mass, containing crystals somewhat triangular in form, which were very insoluble in both water and hydrochloric acid. This substance was not pure and was not further investigated.

Iron-rubidium Alum and Iron-cæsium Alum, $RbFe(SO_4)_2.12H_2O$ *and* $CsFe(SO_4)_2.12H_2O$. — As no description of these alums was found in chemical literature, they were both formed and analysed. In working with rubidium and cæsium salts, a smaller form of apparatus was used, the positive pole being a platinum crucible of 11 c.c. capacity, the negative pole a coil of heavy platinum wire, and the diaphragm an unglazed porcelain annealing cup. The cup was filled as above with a solution of ferrous sulphate, and the platinum crucible, which rested in a ring of heavy copper wire, with a solution of ferrous sulphate and rubidium sulphate or cæsium sulphate. Both solutions were strongly acid with sulphuric acid. Very considerable crops of both the rubidium and cæsium alums were obtained in the form of small octa-

* Read at the Boston meeting of the American Chemical Society, August, 1898. From the *Journal of the American Chemical Society*, vol. xx., No. 10.

hedra. They are of a delicate violet colour, turning slightly greenish on exposure to the air. They resemble potassium-alum in every respect, except that the rubidium alum is very slightly soluble and the cæsium alum almost insoluble in water.

Analysis.

	Calculated for $RbFe(SO_4)_2.12H_2O$.	Found. I.	Found. II.
H_2O	39·3	39·1	38·9
SO_4	34·9	35·2	—
Fe	10·2	11·0	—

	Calculated for $CsFe(SO_4)_2.12H_2O$.	Found. I.	Found. II.
H_2O	36·2	36·1	36·3
SO_4	32·2	33·3	—
Fe	9·4	10·4	—

b. Cobalt Alums.—The cobalt, potassium, and ammonium alums were discovered by Marshall (*Proc. Roy. Soc. Edin.*, xiv., p. 203; *J. Chem. Soc.*, lix., p. 760), whose work was the incentive to that described in this paper. The rubidium and cæsium alums were made by us and have not been hitherto described. The apparatus used was the smaller form, as for the iron rubidium alum, and the experiments conducted similarly. The outer (positive) solution was kept quite strongly acid with concentrated sulphuric acid. Four Bunsen cells were used; current 0·16 to 0·19 ampère. At first it was found that in some experiments beautiful crystals were obtained in considerable quantity, in others no crystals at all. This was soon found to be due to the temperature. On nights when the laboratory was cool the crystals formed readily. By keeping the crucible with its support immersed in a beaker of water, ill effects from heating by the current were avoided and the alums readily obtained.

It is thus seen that the rubidium and cæsium alums are much more readily formed than the potassium and ammonium, as would be expected. These alums are minute, deep blue octahedra, stable in dry air, but gradually decomposing in moist air with formation of cobalt sulphate; the cæsium alum showed occasional cube faces. In water the alums are quickly decomposed with evolution of oxygen and reduction to cobalt sulphate. In dilute hydrochloric acid and in dilute sulphuric acid the crystals dissolve to a blue solution. In concentrated hydrochloric acid and concentrated sulphuric acid they are decomposed, giving in the latter case a brown solution.

Several methods of analysis were tried. On heating to 200° the salt becomes whitish pink, and apparently contains free sulphuric acid from its decomposition into cobalt sulphate, more or less water being thus retained. The best method of analysis was found to be the following:—The salt is mixed with anhydrous sodium carbonate in a platinum boat, and heated in a combustion tube in an oxygen stream. The water is absorbed in a calcium chloride tube. The residue is treated with hot water. The filtrate contains the Cs (or Rb) and the SO_4, which are estimated as cæsium chloroplatinate and barium sulphate. The insoluble residue, cobalt oxide, is heated in a hydrogen stream and weighed as metallic cobalt.

	Calculated for $RbCo(SO_4)_2.12H_2O$.	Found. I.	Found. II.
Rb	15·5	15·9	—
Co	10·7	11·9*	—
SO_4	34·8	35·4	—
H_2O	39·1	37·9	38·2†

	Calculated for $CsCo(SO_4)_2.12H_2O$.	Found.‡
Cs	22·1	22·5
Co	9·8	10·2
SO_4	32·0	32·2
H_2O	36·0	36·7

* $AsCoSO_4$ after removal of Rb as Rb_2PtCl_6.
† By loss at 200°.
‡ By method described above.

c. Chromium Alums.—An experiment was tried using a solution of potassium chromate strongly acidified with sulphuric acid as electrolyte for the negative pole, and dilute sulphuric acid for the positive. After thirty-six hours no chrome alum was obtained, but considerable potassium sulphate was deposited, strongly coloured green by the chromic solution present. On substituting ammonium chromate for the potassium chromate a considerable crop of chromium ammonium alum crystals was obtained at the negative pole. These crystals were very small. Four Bunsen cells were used in these experiments. This method of electrical reduction has been used by Piccini for the formation of vanadium (*Gazz. Chim. Ital.*, xxv., [2], 451) and titanium (*Ibid.*, xxv. [2], 542) alums.

d. Experiments with Manganese.—These experiments were carried out in both the large and small apparatus; with manganese sulphate and ammonium, rubidium, and cæsium sulphates; with varying quantities of free sulphuric acid in the electrolytes; with different strengths of current; and at various temperatures. The solution at the positive pole in every case became deep wine colour, and the higher oxide of manganese was deposited. In one case only were a few minute octahedral crystals found in a rubidium manganese solution. These were deep wine colour, and qualitatively contained manganese. It is not, however, improbable that these were crystals of common alum coloured by manganese. In an experiment with ruthenium such crystals were obtained, the aluminum being probably derived from the porcelain diaphragm. In a number of cases the black precipitate at the positive pole, supposed to be manganese dioxide, when allowed to stand with concentrated sulphuric acid, showed itself under the microscope to be made up of flat, transparent, pale, wine-coloured crystals, resembling elongated hexagonal plates. These are not readily soluble in water or acids. They were not further investigated.

The electrolytical method does not seem to be applicable to the formation of manganese alums from manganous salts.* It is hoped later to try the electrolytic reduction of manganates and permanganates.

e. Experiments with Ruthenium.—No crystallised oxysalts of ruthenium are known. As the double salts of the trichloride crystallise well, an effort was made to obtain an alum by the electrolytic reduction of the nitrosochloride. The small apparatus was used. The solution at the negative pole was a solution of cæsium ruthenium nitrosochloride, Cs_2RuCl_5NO (IV), which had been boiled some time with sulphuric acid, and which might be supposed to contain the nitrososulphate. It was hoped to reduce the nitroso group and split it off as ammonia, leaving trivalent ruthenium in the presence of sulphuric acid and cæsium sulphate, the most favourable condition for alum formation. No sign of alum was found, nor did the electrolysed solution show reaction for trivalent ruthenium. A considerable quantity of ruthenium tetroxide, RuO_4, was given off. This was probably owing to oxidation at the positive pole, some of the ruthenium solution having penetrated the diaphragm into the sulphuric acid which surrounded the positive pole. The formation of ruthenium tetroxide by electrolytic oxidation has not been previously noticed. Further experiments with other ruthenium compounds are being carried on.

* Since the above was in type, a further article by Piccini has appeared in the *Zeitschrift für Anorganische Chemie*, xvii., 361, describing the formation of the cæsium manganese alum by electrolytic oxidation, in a method apparently like that described in this paper. No particulars regarding current, &c., are given. This would seemingly settle the question of the trivalence of manganese in manganic salts. Attention is called, as in our paper, to the advantage in using rubidium and cæsium compounds where it is desired to obtain difficultly crystallisable compounds. Piccini's result renders it probable that the few octahedra obtained in our rubidium manganese experiment were really rubidium manganese alum; he also found his alum contaminated by aluminum from the diaphragm.

THE TRANSITION TEMPERATURE OF SODIC SULPHATE, A NEW FIXED POINT IN THERMOMETRY.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 230).

Third Problem.—The Effect of Varying the Mass of the Phases.

THEORETICALLY, of course, a change in the relative amount of the phases should cause no difference in the nonvariance of the point under consideration provided that no one phase totally disappears. But since the superficial area of either solid present is a factor in determining the speed of the adjustment of the equilibrium, it was thought that varying proportions might cause a slightly varying "temperature lag." Nevertheless, as a matter of fact, no reasonable increase in the amount of either of the solids or of the liquid seemed to cause the least effect, provided that the process was one of melting and not of solidifying, and the mixture was properly stirred. The Beckmann thermometer remained always at 4·760 as long as the barometer stood near to the normal height. In order to insure the rapid establishment of the equilibrium it was our custom to have always some anhydrous powder present in the first place. This precaution also renders harmless drops of water introduced on the washed thermometer or the stirrer. It is well to powder also the hydrated salt, or at least to use it in the form of fine crystals, so as to increase its surface.

Since the point in question seems then to fulfil all the requirements of an accurate standard of reference, manifestly its relations to the international standard should be established.

II. *Reference to the International Standard.*

The only good thermometers indicating 33° at hand in the chemical laboratory are two of a set (one of which has already been mentioned) made by Baudin, and these have not been accurately calibrated. On one occasion thermometer Baudin No. 9389 indicated 32·570° as the point in question, and immediately afterward came to 0·097° in pure melting ice, a difference of 32·473°. Subsequently the same thermometer indicated a change of 32·560 − 0·086 = 32·474°; while the other thermometer (No. 9390) gave on two successive trials, separated by perhaps a week, 32·560 − 0·084 = 32·476°, and 32·550 − 0·083 = 32·467°. The mean of all these values is 32·472°, and to this about 0·009 (see tables by Rimbach in "Landolt und Börnstein," page 143) must be added to correct for the column of 10° exposed to the temperature of the room (about 26°). No other corrections are possible, and there is no further guarantee of the accuracy of the number 32·481° than the evident care used in the construction of the thermometers and the fact that they agree very closely. It is probable that the instruments were made to be used vertically, hence no correction to the horizontal position is needed.

In order to decide more definitely the exact value, Prof. Sabine was so kind as to bring from the Jefferson Physical Laboratory of Harvard University two of the admirable standards in use at that institution. These two instruments, the thermometers Nos. 11,142 and 11,143 of Tonnelot, have been subject to extremely minute scrunity and calibration. They are of course accompanied by a very detailed report from the Bureau Internationale des Poids et des Mesures, and upon this are based all the corrections recorded below, except the last. This one, necessitated by the fact that the thermometers were not wholly immersed in the constant mixture, was calculated from the relative cubic expansion of glass and mercury. The length of the column exposed to the temperature of the room (25·5°) was estimated carefully with the help of another thermometer, and was found to be about 22°, allowing for the conductivity of the glass and mercury. The correction, 0·024, agrees closely with Rimbach's (*loc. cit.*) empirical values, although his were not intended for such small corrections; probably it is not more than 0·003° in error.

Both thermometers are about 6 decimetres long, and have their hundred degrees divided into tenths. With the help of the accurate Geneva cathetometer employed, they could probably be read to within 1/500°. The readings were made with the co-operation of Prof. W. C. Sabine.

The Transition Temperature of Sodic Sulphate.

	Thermom. 11,142 Tonnelot.	Thermom. 11,143 Tonnelot.
Reading at transition point	+32·400	+32·498
Reading in meling ice	+ 0·120	+ 0·101
Uncorrected difference	+32·280	+32·397
Correction for calibration	+ 0·147	+ 0·028
" " interior press (32°)..	+ 0·0330	+ 0·0328
" " " " (0°) ..	− 0·0076	− 0·0075
" " exterior press (32°)	− 0·0006	− 0·0006
" " " " (0°)	+ 0·0007	+ 0·0007
" size of divisions	+ 0·0104	+ 0·0059
" for projecting column..	+ 0·024	+ 0·024
Transition point according to mean Parisian mercury thermometer..	+32·487	+ 32·480

The purest sodic sulphate, and ice from water which had just been twice distilled in platinum (from permanganate, and then from a trace of acid potassic sulphate) were used, and the usual precautions of all kinds were taken. The readings were made with the thermometers vertical: they are reduced to the horizontal position above. The corrected barometer stood at 761 m.m. during the higher readings, and at 762·5 when the thermometers were in ice. The middles of the bulbs were about 45 m.m. below the surface of the inverting mixture, and about 37 m.m. under the ice water. The pressures corresponding are about 4·5 m.m. and 5·7 m.m. of mercury respectively. The sum total of the corrections for exterior pressure is wholly insignificant; they are included above only for the sake of completeness. One division of No. 11,142 equals 1·000320 standard mercury degrees, while one of No. 11,143 equals 1·000181 degrees.

The two results (32·487° and 32·480°) are probably as nearly equal as could be expected, considering that three of the four readings unfortunately fell on dividing lines.

The agreement of the average 32·484 with the result 32·481, obtained from Baudin's uncorrected instruments, is notable; evidently the empirical graduation of the older day included a close approximation to most of the corrections. The result of Löwenherz, 32·39°, is the only previous value with which it is worth while to compare this, but his was meant only for relative work, and was referred merely to "a normal thermometer" of uncertain origin.

While it would be unsafe to predict the precise limit of error of the final value 32·484° (or 32·379 referred to the hydrogen thermometer) the result is certainly near enough to the truth to be a great boon to those who have not a standard instrument at their disposal. If, as is usually the case, it is only desired to attain a result accurate to within 1/100 degree, the thermostat is unnecessary. Surprisingly accurate results may be obtained in the ordinary Beckmann freezing-point apparatus, if the outer bath is a degree or two above the point desired (see *ante*). In fact, it is really an easier point to use than either of the old points, for one can keep neither ice nor steam always at hand in a bottle. Probably the inversion temperature might be of great use as a means of maintaining large vessels at a perfectly constant temperature;

* From the *American Journal of Science*, vol. vi., 1898; also *Zeitschr. Phys. Chem.*, xxvi., 691.

this point deserves consideration. Moreover, while sodic sulphate has several advantages as a standard, there are undoubtedly many other substances which would also serve at other temperatures. One of these, calcic nitrate, inverting at about 42·7°, is at present under investigation at this laboratory, and it is hoped that a complete temperature-scale of standards may be established. It is also hoped that with an admirable new air-thermometer, at present nearly finished in the Jefferson Physical Laboratory, a direct determination of the transition temperature of sodic sulphate may be made in terms of the hydrogen standard.

In brief, this preliminary paper shows that sodic sulphate "melts" at almost exactly 32·48° according to the mean mercury thermometer, and that this temperature is so easily obtained and so constant as to be of great use in the future of thermometry and thermostatics.

THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.*

By W. F. HILLEBRAND.

(Concluded from p. 228).

The Colorimetric Apparatus and its Use.

The glasses employed were of approximately square section, about 12 c.m. high and $3\frac{3}{16}$ c.m. inside measurement, with exactly parallel sides, and of course as nearly alike as they could be obtained. One pair of opposite sides of each should be blackened. With glasses of the thickness mentioned it is generally advisable to use from 5 to 10 c.c. of standard at a time, and to so regulate the strength of the solution to be tested that it shall contain more than 2 m.grms. chromic oxide in 100 c.c., which is about the limit of distinct visibility in a thickness of $3\frac{3}{16}$ c.m.

In order to exclude the effect of side light in this and other similar methods (titanium, for instance), it is very convenient to have a simple light box that can be easily held in one hand, about 35 c.m. long and 13 to 14 c.m. square, painted black inside and out and with one end closed by a piece of ground glass, the other open. For a space equal to the width of the glasses the cover is removed at the top next the glass end, to permit of the insertion of the glasses, side by side, in such a way that no light shall penetrate around their sides or between them. A stiffly-sliding black cardboard shutter is movable up and down immediately back of the glasses, so that all light can be cut off except that which comes through the liquid.

Precautions of this kind are necessary if accurate results are to be counted on. Except for mere traces, this simple combination of glasses and darkened box ensures greater accuracy and rapidity of work than Nessler tubes and is preferable likewise, so far as my own experience goes, to expensive instruments like the colorimeter of Soleil-Duboscq, &c. The glasses should, of course, have exactly parallel sides and equal diameters, though they may perhaps be made with advantage rather narrower in one direction to permit of using smaller bulks of liquid.

In making the colour comparisons, the box is best held close to a window, so as to get a full strong light. The condition of the light seems to make an appreciable difference in the accuracy of the comparisons, all of which were made by daylight.

Accuracy of Results.

Especially for comparatively and very small amounts of chromium the method gives exact results, better than can ordinarily be hoped for from any gravimetric method, considering the fact that, as a rule, other substances are present which it is extremely difficult to remove completely.

A few comparisons between colorimetric and gravimetric determinations of chromium in a few rocks are here given to show the order of agreement, the former having been made several months and even years after the latter.

Gravimetric. Per cent.	Colorimetric. Per cent.
Trace	0·018
0·05	0·051
0·14	0·12
0·08	0·083
Trace	0·013
None	0·0086
None	0·0067

The outcome was somewhat of a surprise, for it was scarcely to be expected that the long and laborious gravimetric separations should have resulted so well as they are shown to have done. It should be mentioned that, for the gravimetric tests, but one or two grms. at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of colour in the aqueous extract of the alkaline fusion after removal of manganese.

No experiments have been made with high percentages, but the tables give with certainty the degree of accuracy even then attainable. Whether the chromic oxide to be estimated is one-tenth per cent or 100 per cent, the percentage result is the same provided the dilution is alike in each case. For instance, if 99·5 per cent is found in a total solution of 100 c.c. containing 0·01 grm. chromic oxide, the same percentage holds if the total volume were ten litres holding 1 grm. chromic oxide.

It is probably inadvisable to increase the strength of the standard much above that of No 2 above, containing two-tenths m.grm. chromic oxide in form of potassium chromate to the cubic centimetre.

No tests have been made with other alkaline solutions than sodium carbonate, in order to ascertain if there is a difference in the colour intensities for like dilution, nor is it probably important to do so.

* Read before the Washington Section, March 10, 1898. From the *Journal of the American Chemical Society*, xx., No 6, June, 1898.

ON THE DETERMINATION OF MANGANESE AS THE PYROPHOSPHATE.*

By F. A. GOOCH and MARTHA AUSTEN.

For the estimation of manganese in a gravimetric way when accuracy is a consideration, recourse is usually taken to the excellent method of Prof. Wolcott Gibbs (*Am. Journ. Sci.*, xliv., 216). This method consists in the precipitation of a manganous salt by an alkaline phosphate, the conversion of the tribasic phosphate into the ammonium manganese phosphate, and the weighing of the product of ignition as the pyrophosphate.

By Dr. Gibbs's original method the orthophosphate of manganese was precipitated by hydrogen disodium phosphate in large excess above the quantity required to cause the precipitation. The flocky white precipitate was dissolved either in sulphuric or hydrochloric acid, and precipitated again at the boiling temperature by ammonia in excess. This semi-gelatinous precipitate on boiling or long standing even in the cold becomes crystalline, the crystals forming beautiful talcose scales which have a pearly lustre and a pale rose colour. The precipitate was filtered off, washed with hot water, dried, and ignited. The results obtained by Dr. Gibbs's students for the pyrophosphate accord closely with the theory.

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1898, vol. vi., p. 233.

Fresenius (*Zeit. für Anal. Chem.*, vi., 415) showed subsequently that ammonium manganese phosphate dissolves in cold water, in hot water, and in an aqueous solution of ammonium chloride (1 : 70) to the extent of one part in 32,000, 1 part in 20,000, and 1 part in 18,000 respectively.

It is clear, however, that the solubility of this precipitate is not indicated necessarily by the proportions given so long as an excess of the precipitant is present during the washing, though Fresenius did find in the filtrate traces of manganese which to his mind were sufficient to account for losses indicated by his test analyses, viz., 1 to 3 m.grms. of oxide, or from 2 to 6 m.grms. of phosphate.

Another mode of manipulation has been advocated by Blair ("The Chemical Analysis of Iron," p. 106) in order that the precipitate may be obtained more easily in crystalline condition. According to this method, dilute ammonia is added drop by drop, to the hot acid solution until the precipitate begins to form, the boiling and stirring are continued until the small amount of flocky precipitate is converted completely to crystalline condition, and the process of adding ammonia drop by drop is repeated until the manganese is all down in crystalline condition. The dilute ammonia is added in excess and the liquid filtered after cooling in ice-water.

In discussing these methods of precipitation, McKenna (*Jour. Anal. Chem.*, v., 141), points out that both give good and accordant results, and that the process may be carried on in glass as well as in platinum, if the time of crystallisation is made short enough.

When a manganous salt is precipitated in the cold by an excess of an alkaline phosphate, it falls, as Heintz (*Pogg. Ann.*, lxxiv., 449), has shown, in the form of the trimanganous phosphate of the formula $Mn_3P_2O_8$. This same phosphate constitutes, as we have found, the greater part of the precipitate which forms when a manganous salt reacts in the cold in the presence of ammonium chloride with microcosmic salt and ammonia in slight excess. Boiling or even subsequent standing may, as is well known, effect a more or less complete conversion of the manganese phosphate to the ammonium manganese phosphate. Thus, in one experiment in which an amount of manganous chloride enough to produce 0·2214 grms. of the pyrophosphate was precipitated in the cold by 5 c.m.^{3} of a saturated solution of microcosmic salt, with the subsequent addition of ammonia in excess, in a volume of 200 c.m.^{3} containing also 5 grms. of ammonium chloride, the residue after ignition weighed 0·1904 grms. Presuming this residue to consist entirely of the pyrophosphate and the trimanganous orthophosphate, the proportion of the former to the latter calculated from the relation of symbols, and the weights taken and found, is nearly one to six. That is to say, about six-sevenths of the precipitate fell in this experiment in the form of the tribasic orthophosphate. In another experiment made exactly similarly, excepting that the liquid was heated to boiling, the proportion of the manganese pyrophosphate to the trimanganous orthophosphate in the only partially crystallised precipitate proved to be two to one. That is, in this case, two-thirds of the precipitate was in the form of the pyrophosphate. In the former of the experiments a small amount of manganese was found in the filtrate, but not enough to change materially the ratio recorded. The slight solubility appears to be connected with the incomplete conversion of the trimanganous phosphate to the ammonium manganese phosphate, for, as will appear later, the manganese found in the filtrate, when the conversion is known to be nearly complete, is inappreciable unless extraordinary amounts of the ammonium salt are present. The success of the analytical process under discussion turns, therefore, upon the change of the trimanganous phosphate $Mn_2P_2O_8$ to the ammonium manganese phosphate NH_4MnPO_4. In the work to be described the attempt was made to learn the conditions under which this conversion may be best and most completely accomplished.

The conversion of a molecule of trimanganous phosphate to the ammonium manganese phosphate might be due, conceivably, either to the action of free ammonia or to the action of a salt of ammonium. The action of ammonia could only take place at the expense of a partial loss of manganese from the phosphate and its appearance as a hydroxide, two-thirds of the manganese going into two molecules of the ammonium manganese phosphate. In the presence of ammonium salts it is possible that the manganese oxide thus replaced might enter into union with the acid radical of the ammonium salt setting free ammonia; but if the ammonium salt present were the phosphate, or if an alkaline phosphate were present with other suitable ammonium salts, it is conceivable that the replaced manganese might appear as a constituent of a third molecule of ammonium manganese phosphate. In any event, it would be the ammonium salt and not the free ammonia which would determine the formation of the third molecule of the ammonium manganese phosphate. Plainly, too, the ammonium salt by itself, if it were a phosphate, or if a soluble phosphate were also present, might accomplish the conversion without the intermediate action of free ammonia. Unless, therefore, free ammonia favours the insolubility of the ammonium manganese phosphate, its presence would be unnecessary and might even be an actual disadvantage if the hydroxide naturally formed by its action upon the manganese phosphate were to fail to reunite fully with a phosphoric acid radical. It is plain, too, that the action of free ammonia might not stop with the replacement of one out of the three of the manganese atoms present in the molecule, but might even proceed under favourable conditions to the formation of phosphate richer in ammonium and to the separation of more manganese from its union with the acid radical. As a matter of fact Monro (*Am. Chem.*, 1877), has shown that the prolonged action of hot ammonia upon the precipitate produced by the interaction of a manganous salt and an alkaline phosphate does actually produce a hydroxide which blackens as it takes oxygen from the air. Our attention has been given, therefore, more especially to a study of the conditions of action under which a salt of ammonium —the chloride—may bring about the conversion of the precipitate first thrown down by an alkaline phosphate to the form of the ammonium manganese phosphate. Experiments were made upon solutions of pure manganous chloride prepared and standardised by means of the sulphate method, as described in a former paper (*Am. Journ. Sci.*, IV., v., 209), to show the effect of varying amounts of ammonium chloride on the condition of the precipitate and upon the solubility of the precipitate when once formed. The ammonium chloride for this work was prepared pure by boiling the chemically pure salt of commerce with a faint excess of ammonium hydrate and filtering—to free it from traces of iron, silica, and alumina. In the first series of experiments dilute ammonia was added slowly to the hot faintly acidulated solution containing the manganous chloride and more than enough, theoretically, of a saturated solution of microcosmic salt to precipitate the manganese present. The liquid was heated and stirred until the flocky mass was changed to a crystalline condition. The addition of ammonia drop by drop, with constant stirring and heating, was continued until the manganese was all precipitated in crystalline form. A slight excess of ammonia was added and the liquid with the precipitate was allowed to stand for half an hour, cooling gradually or chilled in ice water. The precipitate was filtered off on asbestos under pressure, washed carefully in water made faintly ammoniacal, dried, and ignited. The filtrates were tested for manganese by treatment with bromine and heating. The results of these experiments are given in Table I.

In this method of precipitation of the manganese in a pure solution of a manganous salt the results are all wrong. The proportion of the trimanganous phosphate to the pyrophosphate in the residue, calculated from the

TABLE I.

$Mn_2P_2O_7$ equivalent to $MnCl_2$. Taken. Grm.	Found. Grm.	Error in terms of $Mn_2P_2O_7$. Grm.	Error in terms of manganese. Grm.	Saturated solution of $HNH_4NaPO_4.4H_2O$. C.m.³.	Total volume. C.m.³.	Manganese in filtrate.
0·4033	0·3769	0·0264 –	0·0102 –	5	60*	None
0·4033	0·3728	0·0305 –	0·0118 –	5	60*	,,
0·3770	0·3530	0·0240 –	0·0090 –	5	60	,,
0·3770	0·3620	0·0150 –	0·0058 –	5	60	,,
0·4033	0·3751	0·0282 –	0·0109 –	10	60	,,
0·4033	0·3774	0·0259 –	0·0100 –	10	60	,,
0·4033	0·3871	0·0162 –	0·0062 –	5	200	,,
0·3226	0·3066	0·0160 –	0·0062 –	5	200	,,

* Chilled in ice-water.

TABLE II.

$Mn_2P_2O_7$ equivalent to the $MnCl_2$. Taken. Grm.	Found. Grm.	Error in terms of $Mn_2P_2O_7$. Grm.	Error in terms of manganese. Grm.	Saturated solution of $HNaNH_4PO_4.4H_2O$. C.m.³.	NH_4Cl. Grms.	Total volume. C.m.³.	Time of standing cold. Hours.	Manganese in the filtrate.
			A.					
0·1542	0·1520	0·0022 –	0·0008 –	5	5	200	15	None
0·1542	0·1540	0·0002 –	0·0000 –	5	10	200	15	,,
0·1542	0·1536	0·0006 –	0·0002 –	5	10	100	5	,,
0·1542	0·1535	0·0007 –	0·0002 –	5	20	200	2½	,,
0·3770	0·3712	0·0058 –	0·0022 –	5	20	200	½	,,
0·3770	0·3724	0·0046 –	0·0018 –	5	20	200	½	,,
0·3084	0·3069	0·0015 –	0·0006 –	5	40	200	1	,,
0·3084	0·3060	0·0024 –	0·0009 –	5	40	200	1	,,
0·3084	0·3059	0·0025 –	0·0009 –	5	40	200	15	Trace
0·3084	0·3057	0·0027 –	0·0010 –	5	60	200	15	None
			B.					
0·1542	0·1521	0·0021 –	0·0008 –	5	10	100	40	None
0·1542	0·1512	0·0030 –	0·0010 –	5	10	200	40	,,
0·1542	0·1532	0·0010 –	0·0003 –	5	20	200	15	,,
0·1542	0·1531	0·0011 –	0·0004 –	5	20	100	15	,,
0·3770	0·3720	0·0050 –	0·0019 –	5	20	200	½	,,
0·3770	0·3745	0·0035 –	0·0014 –	5	20	200	½	,,
			C.					
0·1542	0·1519	0·0023 –	0·0009 –	5	15	200	—	None
0·1542	0·1530	0·0012 –	0·0004 –	5	20	200	—	,,
0·1542	0·1525	0·0017 –	0·0007 –	5	30	200	—	,,
0·3084	0·3020	0·0064 –	0·0025 –	5	10	200	—	,,
0·3084	0·3053	0·0031 –	0·0012 –	5	20	200	—	,,
0·3084	0·3033	0·0051 –	0·0020 –	5	20	200	—	,,
0·3084	0·3039	0·0045 –	0·0017 –	5	60	200	—	Trace

symbols and the weights taken and found, is in the average two to five; that is to say, five-sevenths of the trimanganous phosphate has been converted to the form of the ammonium manganous phosphate.

The precipitate obtained in this manner is white and granular, but not silky, and after ignition it shows the same dead white colour and is powdery. Evidently the regulation of the volume in which the precipitation is made is not essential, and the chilling of the liquid is of no importance in changing the manganese to the ammonium manganese salt under the given conditions. It is plain, moreover, that the assumption of a crystalline condition cannot serve as an indication that the composition of the salt is ideal. It is to be noted, however, that the conditions obtaining here are essentially different from those in common practice; for, ordinarily, when manganese is to be determined ammonium salts are abundantly present as the result of previous steps in analysis.

In the experiments of the next series the conditions are varied simply in this respect, that ammonium salts are introduced before the precipitation. The precipitate was less granular and more silky. After ignition the mass was white with a faint rose colour. In the experiments of Section A (Table II.) the precipitate first thrown down was re-dissolved, re-precipitated, and filtered after cooling; in those of Section B, the precipitate was filtered after cooling without re-solution and without re-precipitation; and in those of Section C, the first precipitate was filtered at once while the solution was still hot. The length of digestion before filtering and the indications of manganese in the filtrate are recorded in the table.

It was observed in these experiments that when the amount of ammonium chloride is present in considerable quantity a fine crystalline condition is got much more readily than when the amount of that salt is small: with maximum amounts of ammonium chloride the change from the flocky to the crystalline condition is almost immediate; even in the cold the change takes place to a marked extent in a few seconds. No manganese was found in the filtrate by boiling with bromine and ammonia —a test which is capable of indicating 0·0001 grm. of manganous sulphate in 500 c.m.³ of water containing 60 grms. of ammonium chloride—until the ammonium chloride amounted to 20 per cent of the mass, or to 40 grms. in 200 c.m.³ of the liquid, and even then but once in three trials: even when the proportion was 30 per cent —60 grms. in 200 c.m.³—the solvent action of the ammonium chloride upon the manganese salt was trifling. The pyrophosphate residues obtained in these experiments, as well as in all those recorded in this paper, were dissolved in nitric acid and tested for contamination by a chloride; in no single case did silver nitrate produce more than an inappreciable opalesence in the solution. It is plain, therefore, that the variations of the results from theory are occasioned by variation in the degree of conversion of the trimanganese phosphate to the ammonium

manganese phosphate, and that while the ammonium chloride shows no appreciable solvent action on the precipitate in the presence of the precipitant, its effect in the process of conversion is plainly evident. For the smaller amounts of the manganese salts (equivalent to 0·1542 grm. of the pyrophosphate) the effect of the ammonium chloride reaches a maximum when that salt amounts to 10 per cent of the solution; for twice that amount of manganese salt, the best results were obtained by doubling the amounts of ammonium chloride. Either line of treatment yields under the most favourable conditions, results which are passably good, but the advantage inclines slightly to the first method in which the first precipitate was dissolved and re-precipitated while the liquid was cooled before filtering.

(To be continued).

NOTICES OF BOOKS.

Arithmetical Chemistry. Part I., New Edition. By C. J. Woodward, B.Sc. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd.

This little book sets forth, in simple language, the principles underlying the science of chemistry, and at the same time insists on the necessity of every pupil, even the youngest beginner, performing for himself such experiments as illustrate the principles dealt with in the text. After working conscientiously through this book, every student should be familiar with the arithmetical calculations involved in both quantitative and qualitative analysis.

It is to be regretted that the author does not distinguish between mass and weight. The statements on pages 15 and 42, if taken literally are irreconcilable. The confusion of terms is liable to involve the student in a confusion of ideas, which may easily lead to serious errors.

General Elementary Science. By William Briggs, M.A., F.R.A.S., F.C.S. Second Edition. London: W. B. Clive.

This volume forms part of the "University Tutorial Series" now being issued by Cambridge University. It treats, in simple language, of the elementary principles of Mechanics; Heat, Light, and Electricity; and Chemistry.

A handy volume, primarily intended for the use of Matriculation candidates, and should be useful to a larger circle of students.

The Organised Science Series. Second Stage Mathematics. Edited by William Briggs, M.A., &c. London: W. B. Clive.

This book is compiled specially to meet the needs of students preparing tor the advanced stage of the Science and Art Examinations. Being intended for the use of students without the personal help of a tutor, the various problems and theorems are worked out with an unusual amount of detail, and any ordinary student should with this guide be able to pass the examination with ease.

Section I., dealing with Euclid, Books II., III., and IV., calls for no comment, excepting that an alternative solution to Prop. I., Book III., on page 39, is not valid, since it is not known at this stage that more than two of the lines bisecting chords of a circle at right angles meet at the same point. Exercise 6, on page 43, is curiously worded; in fact, as it stands it has no solution, since, in general, a circle cannot be described through four given points.

Section II. deals with Algebra, chiefly quadratic equations. This section should be carefully edited in future editions, and the misplaced and dropped signs—especially numerous in Chapter 4—corrected.

Section III. treats of the elements of trigonometry and the principles and use of logarithmic tables in a clear manner, though this section could with advantage be compressed.

On the whole the work is well adapted to its purpose, though there is room for improvement in future editions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 26, June 27, 1898.

Action of Hydrogen on Sulphide of Silver and the Inverse Reaction.—H. Pélabon.—The author investigates the reaction of sulphuretted hydrogen and silver or of hydrogen and silver sulphide contained in sealed tubes at a fixed temperature. After a measured time the tube is quickly cooled and the gases are analysed. He finds (1) that for temperatures above 350° C. the limiting values for the proportion of sulphuretted hydrogen in the mixture are identical, whether the tube originally contained H_2S and silver or Ag_2S and hydrogen; and (2) that equilibrium is obtained in a time, increasing as the temperature is lowered. The silver is deposited in the form of threads when the temperature is below 580°; at higher temperatures the particles of silver sulphide are seen at the end of the experiment to be covered with an almost uniform layer of metallic silver.

Heat of Formation of Lithium Carbide.—M. Guntz.—This is found by measuring the heat evolved by the solution of a known weight of lithium carbide in water—

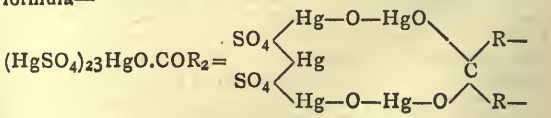
$$C_2Li_2 + 2H_2O = 2LiOH + C_2H_2.$$

The number found (37·1 cal.) is the mean of three determinations. In order to avoid the correction due to the solubility of acetylene in the liquid in the calorimeter, the decomposition takes place in a glass apparatus, plunged into the calorimeter, from which the acetylene escapes freely into the air. The quantity of carbide employed is found each time by titration. The heat formation of Li_2C_2 is much greater than the corresponding values for CaC_2 and NaC_2.

Capacity of Organic Bodies for Combining with Mercuric Sulphates. The Case of the Acetones.—G. Denigès.—In a preceding communication the author has demonstrated the facility with which $HgSO_4$ furnishes well-defined insoluble compounds with thiophene and the ethylene hydrocarbons. The following table enumerates the principal bodies which have yielded such compounds—

Thiophene and its derivatives.
Ethylene, benzene, terpene, and their derivatives.
Aldehyds.
Acetones.

Fatty acetones heated to boiling with large excess of $HgSO_4$ yield bodies insoluble in water corresponding to the general formula—



With ordinary acetone the reaction is absolutely quantitative. Secondary actions occur in the case of acetones richer in carbon.

A General Method for Preparing Mixed Carbonic Esters of the Fatty and Aromatic Series.—P. Cazeneuve and Albert Morel.—Fatianow, Richter, and Bender obtained carbonic esters of ethyl and different phenols by means of the reaction between ethyl chlorocarbonate and phenolates of sodium or potassium. The author has succeeded in producing these mixed carbonates in a more practical way by warming neutral phenolic carbonates with different alcohols in presence of certain organic bases. Phenyl carbonates in particular, warmed with fatty alcohols in presence of urea, give mixed carbonates of phenyl and the alcohol in question. Certain of these esters have been obtained extremely pure, but the higher members are difficult to purify on account of the formation of urethanes. Other bases act similarly to urea without giving rise to these impurities, *e.g.*, aniline, dimethylaniline, pyridine, and quinoline. The double decomposition which occurs is, according to the following equation—

$$CO\langle^{OC_6H_5}_{OC_6H_5} + C_2H_5OH.C_5H_5N = = CO\langle^{OC_6H_5}_{OC_2H_5} + C_6H_5OH.C_5H_5N.$$

The decomposition is hastened by the affinity of the base for phenol. Further, a similar reaction occurs between sodium ethylate dissolved in excess of absolute alcohol and phenyl carbonate.

Vol. cxxvii., No. 1, July 4, 1898.

Decomposition of Water by the Salts of Protoxide of Chromium, and the Employment of these Salts for the Absorption of Oxygen.—M. Berthelot.—At temperatures below 250° a solution of chromous chloride, quite pure and free from all tracs of acid, does not decompose water, even when the two are left in contact for eleven years. At temperatures above 250° the water is decomposed. However, chromous chloride can be made to decompose water at ordinary temperatures. With the help of some outside energy, for example, the slightest addition of HCl, the decomposition takes place even in the cold. This decomposition only proceeds up to a certain point, for after two months the liquid is found still to contain two-fifths of the chromous chloride unaltered.

Action between Free Hydrogen and Nitric Acid.—M. Berthelot.—Hydrogen and nitric acid react on one another in an unexpected way. They exert no reciprocal action in the cold, nor at 100°, even under conditions when nitric acid would decompose of itself, giving off oxygen. A little bulb containing pure nitric acid is put in a vessel filled with hydrogen and sealed off; the bulb is broken and the tube placed horizontal and exposed to solar light for some days. The gases are then examined and the hydrogen is found to be unaltered in amount, the oxygen present being formed by the decomposition of the nitric acid only. An almost equal amount of oxygen is formed if the hydrogen is not present at all. If two similar tubes containing nitric acid are placed in darkness, in one pure hydrogen, the other a vacuum, in neither case does any change take place. This inactivity between nitric acid and hydrogen ceases at a high temperature.

Preparation and Properties of Hydride of Calcium.—Henri Moissan.—The author prepares this substance from pure crystalline calcium, which is put in a nickel boat in a glass tube, through which passes a current of pure dry hydrogen. At ordinary temperatures no action takes place and the hydrogen merely sweeps out the tube. The tube is then sealed off and the hydrogen kept under a pressure of 30 to 40 c.c. of water. The temperature is raised to dull redness, when the calcium is seen to take fire in the atmosphere of hydrogen. The gas is rapidly absorbed and the calcium metal is transformed into white hydride of calcium. The hydride has sp. gr. 1·7 and has the appearance of small thin transparent plates. It is stable up to 600° in a vacuum and has a formula CaH_2.

Blue Glass with Chromium Bases.—André Duboin.—Already inserted.

Seleniate of Copper and its Employment in the Preparation of Selenic Acid.—R. Metzner.—Seleniate of copper is prepared by passing a current of chlorine through an aqueous solution of SeO_2 :—

$$SeO_2 + 2Cl + H_2O = 2HCl + SeO_3.$$

The acid is then neutralised by oxide of copper, when the liquid takes a blue colour. Analysis shows the seleniate of copper to have the formula $2(CuOSeO_3)CuO5H_2O$.

The Phenyl Urethanes of the Ethers and Nitrates of certain Oxyacids.— E. Lambling.— Following the observation of A. W. Hofmann, that phenylisocyanate combines readily with alcohols and phenols to give urethanes, the author proposes to investigate the effect that may be exercised on the alcoholic hydroxyl by the proximity of various acidifying groups, such as C_6H_5, CN, CO, &c. The possible influence of these radicals is studied by the action of phenylisocyanate on bodies of analogous constitution, viz.:—(1) Lactic ether and trichloracetic ether, and nitrile; (2) glycolic ether and nitrile; (3) phenylglycolic ether and nitrile; (4) β-oxybutyrate of ethyl and α-oxyisobutyrate of ethyl. A description of the preparation and composition of the urethanes of these substances is given, and the conclusion drawn that the groups CN, C_6H_5, CO, CCl_3, exercise no sensible influence in the fixation of the phenylisocyanate by the neighbouring hydroxyl; also that it apparently does not matter whether the alcoholic hydroxyl be primary, secondary, or tertiary.

A New Combination of Acetylene with an Oxychloride of Copper, corresponding to the Formula C_2H_2—$Cu_2Cl_2.Cu_2O$.— R. Chavastelon.— The author prepares the compound in two ways :—(1) By allowing a crystal of $C_2H_2.Cu_2Cl_2$ to stand in contact with distilled boiled out water at ordinary temperatures, the change not being complete for several days; (2) by adding to excess of water a solution of $C_2H_2.Cu_2Cl_2$ crystals, or a solution, saturated with acetylene, of Cu_2Cl_2 in hydrochloric acid, in which case an abundant violet flocculent precipitate is at once obtained. The formation of this compound is accompanied by evolution of acetylene and production of free hydrochloric acid, and by determining the quantities of these two substances produced when a known weight of $C_2H_2Cu_2Cl_2$ is treated with water, the composition of the residue is deduced. A more exact method of determining the composition is to analyse the substance formed, which is found to correspond to the formula $C_2H_2.Cu_2Cl_2.Cu_2O$.

Ethane Di-pyrocatechin.—Ch. Moureu.—The author investigates the action of dibrom- and tetrabromacetylene on pyrocatechin in the presence of alkalis. With $C_2H_2Br_2$, spontaneously inflammable C_2HBr is evolved, and no $C_6H_4O_2.C_2H_2$; but with $C_2H_2Br_4$, on the contrary, a well-defined condensation product with pyrocatechin is formed. Its composition agrees with the formula $C_{14}H_{10}O_4$, *i.e.*, ethane-di-pyrocatechin—

$$C_6H_4O_2 = C_2H_2 = C_6H_4O_2,$$

which is formed according to the equation—

$$2C_6H_4\langle^{OK}_{OK} + CHBr_2 - CHBr_2 = = 4KBr + C_6H_4\langle^{O}_{O}\rangle CH - CH\langle^{O}_{O}\rangle C_6H_4.$$

A description of the properties of this substance is given.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The special thanks of the Members were returned to Mr. John B. Carrington, for his donation of £25, and to Mr. Charles Scott Dickson, Q.C., Solicitor-General for Scotland, for his donation of £100 to the fund fer the promotion of Experimental Research at Low Temperatures.

MEETINGS FOR THE WEEK.

Wednesday, 16th.—Microscopical, 7.30. Exhibition of Shum's Slides of Diatoms Mounted in High Refractive Media.

Thursday, 17th.—Chemical, 8. "Preparation of Hyponitrite from Nitrite through Oxyamidosulphonate," by E. Divers, M.D., F.R.S., and T. Haga, B.Sc. "Absorption of Nitric Oxide in Gas Analysis," "Interaction of Nitric Oxide with Silver Nitrate," "Preparation of Pure Alkali Nitrites," "The Reduction of an Alkali Nitrite by an Alkali Metal," "Hyponitrites—their Preparation by Sodium or Potassium and Properties," by E. Divers, M.D., F.R.S.

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THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2034.

THE ESTIMATION OF FORMIC ACID IN THE PRESENCE OF ACETIC ACID, AND OF EASILY OXIDISABLE BODIES.

By ALEXANDRE LEYS.

THE estimation of formic acid in the presence of other organic bodies, such as acetic acid or alcohol, presents difficulties of a special nature. Distillation only effects a partial separation, and the direct use of oxidising agents is in most cases impossible.

M. F. Freyer gave, some years ago, in the *Chemiker Zeitung* (No. 51, 1895), a process for the titration of formic acid in acetic solution; but this process loses all its value when the materials are not absolutely pure, and it is quite inapplicable in the presence of alcohol.*

We have found a reaction which enables us to overcome these difficulties, and to estimate with exactitude formic acid mixed either with acetic acid, methylic or ethylic alcohol, or even with their corresponding aldehyds. There is no doubt that, later on, we shall be able to add to this necessarily limited list.

If we take a solution of acetate of mercury, and pour into it minimal quantities of formic acid, no reaction appears to take place at ordinary temperatures. The mixture remains clear, and it is only after a few hours that pearly-looking scales, of great lightness, begin to deposit in the flask, which must be kept closed to prevent all evaporation. These are crystals of mercurous acetate, of which the deposition increases during from eight to fifteen days, according to the surrounding temperature and the quantity engaged in the reaction. We also noticed that small bubbles of gas become disengaged from the mass.

With larger quantities of formic acid the manner of the reaction does not change; no cloudiness is observed when the mixture with the mercuric acetate is made, but the deposit takes a shorter time to produce, and, instead of forming light pearly flakes, it seems to differ slightly, and takes the form of a white pulverulent precipitate.

This reaction, slow to finish at the ordinary temperature, takes place with rapidity when we heat to boiling. We notice the bubbles of gas, more and more numerous, deposited on the sides of the glass, and the liquid even appears to be boiling, although that temperature may not be nearly reached. The heat must be stopped as soon as boiling commences, and already we see light flaky crystals floating on the surface. On cooling, the whole volume of the liquid becomes full of a mass of crystals with a brilliant white lustre.

The presence of acetic acid, alcohol, or of aldehyd in no way interferes with this reaction, but when their proportions become considerable the volume of the precipitate varies. The crystals are more granular, more dense, and do not occupy the whole space. Nevertheless, repeated analyses that we have made have always shown the same proportion between the acting formic acid and the quantities of mercury found in the state of mercurous salts.

We therefore believe, although we have not yet verified it, that we have to do with two kinds of crystals of mercurous acetate, one of which at least contains a certain quantity of water. But, however this may be, the reaction is always complete when we reach the boiling-point of the mixture; and in fact in the various cases, if we separate the crystals by filtration, the filtered liquid will not become cloudy even after the lapse of several days.

According to our ideas the following is what happens:—The formic acid displaces the acetic acid from the mercuric acetate, and gives a mercuric formate which is unstable and changes spontaneously into mercurous formate. The mercurous formate is in its turn attacked by the acetic acid, and a very slightly soluble mercurous acetate is formed, which crystallises out. This reaction can be shown in the following manner:—

$$_2{}^{CH_3COO}_{CH_3COO}{>}Hg + 4H.COOH =$$

$$= 4CH_3.COOH + 2{}^{H.COO}_{H.COO}{>}Hg$$

$$_2{}^{H.COO}_{H.COO}{>}Hg = {}^{H.COO}_{H.COO}{>}Hg_2 + H.COOH + CO_2$$

$${}^{H.COO}_{H.COO}{>}Hg_2 + 2CH_3.COOH =$$

$$= {}^{CH_3COO}_{CH_3COO}{>}Hg_2 + 2H.COOH.$$

The destruction of a single molecule of formic acid suffices to accomplish this cycle, and 1 molecule of mercurous acetate is deposited.

Let us add that the chief characteristic of this reaction is that it takes place with the smallest quantities of formic acid; 10 m.grms. in a solution of mercuric acetate produce a voluminous precipitate, even in the cold. To easily repeat the experiments we have just described, it is necessary to use solutions of formic acid at 1 per cent; a stronger solution would not give such good results.

We take a Bohemian glass flask gauged to 100 c.c., and pour in 10 c.c. of the acid solution, 20 c.c. of a 20 per cent solution of mercuric acetate, and make up to 100 c.c. with distilled water; then boil, stop the heat as soon as the boiling-point is reached, and allow to cool slowly.

After having recognised by numerous analyses that the precipitation of a molecule of mercurous acetate really corresponded with the destruction of H—CO.OH, and having found a convenient method for weighing the mercurous salt produced, we decided on the following method of estimation, which is perfectly exact:—

The Case of a Mixture of Acetic and Formic Acids.—We commence by the determination of the acidity of the mixture in terms of acetic acid. Here it is necessary to distinguish between two possible cases:—

Case I.—The mixture is rich in acetic acid, and contains only a small quantity of formic acid. We dilute with water until the mixture contains only 20 to 30 per per cent of acids.

Case II.—The mixture reaches the proportion of 1 part of formic acid for 20 parts of acetic acid. For this proportion and for all higher proportions (of formic acid) we dilute with water until the liquid has an acidity of only 2 per cent. Having obtained a sufficiently dilute solution, we take 10 c.c. and place them in a beaker having a mark for 100 c.c. at about one-third of its height, we add 20 or 30 c.c. of a 20 per cent solution of mercuric acetate, and fill up to the mark with distilled water.

The relatively large quantity of mercuric acetate thus present is necessary, for we found that the mercurous salt produced is not stable except in the presence of such an excess. When the proportion is not sufficient it easily decomposes, and becomes of a greyish colour and loses mercury.

We then heat so as to reach the boiling-point in seven or eight minutes; as soon as this temperature is reached we withdraw the flame, and leave the whole to cool until the following day. The product thus obtained is of a

* Besides Freyer's process—which is an application of the experiments made by Chapman and Thorp on the non-oxidation of acetic acid, even at 100°, by chromic acid—there exists a method of estimating formic acid when mixed with acetic acid, which is due to MM. Portes and Ruyssen. This process has been modified by M. Scala (*Gazz. Chim. Ital.*, 1890, p. 393). M. Lieben, who has studied this latter method, gives it the following character:—The reaction is always very slow in finishing, which leads to losses of formic acid. We can only arrive at approximately exact results by using a large excess of mercuric chloride. M. Lieben recommends four times the theoretical weight, or fifty times the weight of the formic acid, and heating for from six to eight hours.

brilliant white colour: it is collected in a funnel plugged with a little glass wool, and the portions adhering to the sides of the beaker are washed in by means of the filtrate which is poured back into the glass in which the reaction took place. When the beaker no longer contains any trace of the precipitate the funnel is allowed to drain; we then wash four or five times with alcohol at 95° containing 2 c.c. per cent of glacial acetic acid. This slight acidity prevents the solution of mercuric acetate which impregnates the crystals from being decomposed by the strong alcohol, and thus permits a complete washing of the deposit. We finish by two or three washings on the funnel with neutral alcohol at 95°, to remove all trace of acetic acid, and we finally get rid of the alcohol with a few washings with anhydrous ether.

The product is allowed to dry either in free air or under a bell-jar *in vacuo*, and we obtain on the funnel a felted mass of beautiful silvery-white crystals, somewhat resembling the flakes of boric acid. These crystals are quickly dissolved in nitric acid diluted with its own volume of water.

To obtain good results it is necessary that the reaction should be almost instantaneous, so as to prevent a slight precipitation of mercury; but, however, even if the precipitate is produced, the quantity of mercury precipitated is so minute that the error may be neglected. Further, this slight loss disappears of itself after standing a few hours.

The funnel and its contents are plunged into nitric acid, then withdrawn and washed thoroughly. Make up to a given volume, and there then remains nothing but to estimate the mercury in the state of a mercurous salt in the solution.

Take 10 c.c. of the solution of mercurous nitrate, dilute with a large quantity of water, and precipitate with a slight excess of chloride of sodium. After standing a sufficiently long time, so that the supernatant liquid may become clear, the mercurous chloride is collected on a tared filter. Wash until the filtrate is neutral, and place the precipitate in an oven at 100°; it is important that the mercurous chloride should not be exposed to the temperature of 100° longer than is absolutely necessary to properly dry it, for we have observed that even at this temperature there is a sensible volatilisation of the substance. The following table will prove this :—

	Weight of precipitate.	Losses.
1st day	0·066 grm.	—
2nd ,,	0·061 ,,	5 m.grms.
3rd ,,	0·056 ,,	10 ,,
4th ,,	0·051 ,,	15 ,,
5th ,,	0·047 ,,	19 ,,

We multiply the weight of the mercurous chloride found by 0·0976 to obtain the corresponding weight of formic acid. The factor 0·0976 is obtained by the following reasoning:—The destruction of 1 molecule of formic acid leads to the precipitation of 1 molecule of mercurous acetate; but for the purpose of estimation this latter was converted into chloride; therefore—

$$474\,x = 46,$$

whence $x = 0{\cdot}0976$.

The different samples of formic acid we have tried have given us results absolutely concordant. We bring them all first to a strength of 1·30 per cent of total acidity; we then take 10 c.c., or 0·130 grm., which we place in the reaction beaker, adding 2 c.c. of glacial acetic acid before completing with the mercury salt and water.

The following is a series of results :—

First result	0·132 grm.
Second ,, ...	0·129 ,,
Third ,, ...	0·1289 ,,
Fourth ,, ...	0·1288 ,,

This table shows the results obtained with a mixture of 2 parts of acetic acid and 0·130 part of formic acid, or, in other words, with an acetic acid containing 93·9 per cent of acetic acid and 6·1 per cent of formic acid. Experiments we have made authorise us to state that we could obtain as exact results with an acid containing 99 per cent of acetic acid and 1 per cent of formic acid.

The Case of a Mixture of Formic Acid and Alcohol.—After having determined the acidity, we dilute with water to bring the liquid to from 1 to 2 per cent. Pour 10 c.c. into the gauged beaker, then before adding the mercuric acetate we add 2 c.c. of glacial acetic acid to check the precipitation. We then proceed as before, and we obtain the substance already described, or, when the proportion of alcohol is considerable, granular, dense crystals of which we have already spoken. In every way the results are just as exact. For 0·130 grm. of acid put in reaction in alcohol at 30° we found 0·129 grm.

The Case of a Mixture of Formic Acid, Acetic Acid, and Alcohol.—We operate as before, but without adding acetic acid when the proportion in the solution is already great.

All that we have said with regard to ethylic or methylic alcohols will apply to their aldehyds pure or mixed with them. We are strongly inclined to think—but as we have not verified it we cannot state definitely—that many other organic bodies could be present without interfering with the reaction.

Without wishing to dwell too long on the applications of which this reaction is susceptible, we will, however, just mention the following :—The determination of small quantities of formic acid which are to be found in certain raw spirits, and by that means detecting adulteration. The determination of quantities of formic acid, which, mixed with acetic acid, are found in commercial formol. A method of titrating formic aldehyd after oxidation. Finally, a method of testing and titrating methylic alcohol mixed with the alcohol in wines, when we are in possession of a method of oxidation which will transform the alcohols into acid without attacking these latter.—*Moniteur Scientifique*, Series 4, xii., Part 2, Sept., 1898.

ON THE DETERMINATION OF MANGANESE AS THE PYROPHOSPHATE.*

By F. A. GOOCH and MARTHA AUSTEN.

(Concluded from p. 242).

In Table III. are recorded results obtained by precipitating the cold acid solution of the manganese salt and the microcosmic salt with a strong excess of ammonia. The mixture was heated to boiling for from five to ten minutes and filtered hot. In this series of determinations the amount of ammonium chloride present was constant, while the volume of the liquid present was varied and the amounts of the microcosmic salt.

These results are possibly a trifle less satisfactory than those obtained for the smaller amounts of manganese by the method of Table II., it may be because the prolonged boiling tends to form a trifling amount of free oxide; but the fact is disclosed that an increase of the microcosmic salt is without influence, and that a variation in volume from 200 c.m.^{3} to 300 c.m.^{3} is the occasion of little change in the indications of the process.

In another series of experiments the solution of manganous chloride was added drop by drop to the mixture of microcosmic salt and ammonium chloride made alkaline with ammonia. The precipitate which fell in the cold was crystallised by boiling the mixture a few minutes. The results are given in Table IV.

The experience of this series of experiments demonstrated again that the ease with which the flocky precipitate is converted to the crystalline ammonium manganese

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1898, vol. vi., p. 233.

TABLE III.

$Mn_2P_2O_7$ equivalent to $MnCl_2$. Taken. Grm.	Found. Grm.	Error in terms of $Mn_2P_2O_7$. Grm.	Error in terms of manganese. Grm.	Saturated solution of $HNaNH_4PO_4.4H_2O$. C.m.s.	NH_4Cl. Grms.	Total volume. C.m.s.	Manganese in the filtrate.
0·2214	0·2202	0·0012 −	0·0005 −	5	20	200	None
0·2214	0·2202	0·0012 −	0·0005 −	5	20	200	,,
0·2214	0·2191	0·0023 −	0·0009 −	5	20	200	,,
0·2214	0·2191	0·0023 −	0·0009 −	5	20	300	,,
0·2214	0·2191	0·0023 −	0·0009 −	5	20	300	,,
0·2214	0·2185	0·0029 −	0·0011 −	10	20	200	,,
0·2214	0·2186	0·0028 −	0·0010 −	20	20	300	,,
0·2214	0·2192	0·0022 −	0·0009 −	20	20	300	,,

TABLE IV.

$Mn_2P_2O_7$ equivalent to $MnCl_2$. Taken. Grm.	Found. Grm.	Error. Grm.	Error in terms of manganese. Grm.	Saturated solution of $HNaNH_4PO_4$. C.m.s.	NH_4Cl. Grms.	Total volume. C.m.s.	Manganese in the filtrate.
0·1542	0·1521	0·0021 −	0·0008 −	5	5	200	None
0·2214	0·2203	0·0011 −	0·0004 −	5	10	275	,,
0·2214	0·2192	0·0022 −	0·0009 −	5	15	275	,,
0·2214	0·2197	0·0017 −	0·0007 −	5	20	275	,,
0·2214	0·2223	0·0009 +	0·0003 +	5	20	200	,,
0·1542	0·1528	0·0014 −	0·0005 −	5	30	275	,,

TABLE V.

$Mn_2P_2O_7$ equivalent to MnO_2. Taken. Grm.	Found. Grm.	Error in terms of $Mn_2P_2O_7$. Grm.	Error in terms of manganese. Grm.	Saturated solution of $HNaNH_4PO_4$. C.m.s.	NH_4Cl. Grms.	Total volume. C.m.s.	Manganese in the filtrate.
			A.—*In Platinum.*				
0·1885	0·1903	0·0018 +	0·0007 +	5	20	200	None
0·1885	0·1910	0·0025 +	0·0010 +	5	20	200	,,
0·1885	0·1913	0·0028 +	0·0011 +	5	20	200	,,
0·1885	0·1911	0·0026 +	0·0010 +	5	20	200	,,
0·3770	0·3776	0·0006 +	0·0002 +	5	20	200	,,
0·3770	0·3773	0·0003 +	0·0001 +	5	20	200	,,
0·3770	0·3778	0·0008 +	0·0003 +	5	20	200	,,
0·3770	0·3783	0·0013 +	0·0005 +	5	20	200	,,
			B.—*In Glass.*				
0·1885	0·1904	0·0019 +	0·0007 +	5	20	200	,,
0·1885	0·1898	0·0013 +	0·0005 +	5	20	200	,,
0·3770	0·3767	0·0003 −	0·0001 −	5	20	200	,,
0·3770	0·3784	0·0014 +	0·0005 +	5	20	200	,,

phosphate is proportioned to the ammonium chloride present, and the mean error of the results for the phosphate when the ammonium chloride reached 20 grms. (−0·0007 grm.) is considerably less than the mean error (−0·0018 grm.) when the amount of the ammonium salt was less than 20 grms.

Experiments were also made according to the modifications suggested by Munroe (*loc. cit.*), viz., the boiling of the manganous salt with an excess of microcosmic salt until the precipitate becomes crystalline and just neutralising with dilute ammonia; but we have been unable to find the conditions of this treatment by which uniform results may be obtained in even moderate agreement with the theory.

We have tried also the effect of substituting ammonium nitrate for ammonium chloride in the conversion process; but, so far as our experience goes, the nitrate is not so effective weight for weight in producing the change of the trimanganous phosphate to the ammonium manganese phosphates, while the solubility of the product in the solution of the ammonium nitrate becomes appreciable more rapidly with the increase of the amount present than is the case when the ammonium salt is the chloride.

In the light of the experiments described it would seem to be reasonable to expect the best results from the phosphate method for determining manganese when the conditions are so arranged that precipitation may take place in the cold solution in the presence of but little free ammonia, and of enough ammonium chloride to bring about the rapid conversion of the precipitate to the crystalline condition. Under such circumstances it should be possible to secure the conversion of the phosphate to the ideal constitution as completely as possible without danger of subsequent decomposition by the prolonged action of the hot free ammonia. In carrying out this idea, the solution of manganese chloride was treated, as before, with microcosmic salt and a large amount of ammonium chloride, the precipitate first formed was re-dissolved in hydrochloric acid, and precipitation again brought about by the very careful addition of dilute ammonia in slight but distinct excess. The mixture was heated only until the precipitate became silky and crystalline, when it was allowed to stand and cool for a half hour. The precipitate was filtered off upon asbestos in a perforated platinum crucible under pressure, ignited, and weighed. Table V. comprises the results of experiments made in this manner. In those of Section A the precipitation was made in platinum vessels; in those of Section B the treatment was in glass.

In this series of experiments the mean indication is, for the first time, in excess of the theory. Previously the error has been one of deficiency, and that in proportion to the amount of manganese handled, no doubt because the amount of unconverted trimanganese phosphate is proportioned to the entire amount of the phosphate. The positive error which is developed in this last series of determinations is probably due to the appearance of the

natural error of all precipitation processes — viz., the tendency on the part of the precipitate to include matter in solution. In the previous experiments this effect was doubtless obscured by the incompleteness of the conversion of the trimanganous phosphate to the ammonium manganese phosphate. Indeed, it is quite possible that even in the last determinations the conversion is not absolute, and that this is so suggested by the fact that the errors of excess are larger in the case of the smaller amounts of manganese for which the conversion throughout the entire work has appeared to be more complete. From the consideration of the results tabulated and described it would seem to be obvious that not only is the presence of ammonium chloride not objectionable in this analytical process, which depends upon obtaining the ammonium manganese phosphate from the trimanganese phosphate precipitated from a pure solution of manganese, but that its presence in not too small amount, or that of a substitute, is absolutely essential to make this conversion complete. For a given amount of manganese and a given volume of solution it seems essential that the amount of ammonium chloride should reach a certain limit. According to our experience the proportion of ammonium chloride to the pyrophosphate should be at least 50 : 1; or, speaking approximately, more than 200 molecules of ammonium chloride must be present in the liquid (100 c.m.^{3} or 200 c.m.^{3}) to every molecule of the ammonium manganese phosphate to be formed. However, the quantity of the ammonium salt may be increased almost to the point of saturation of the liquid without causing more than a trifling solubility of the ammonium manganese phosphate in the presence of an excess of the precipitant. The statement of Fresenius and Munroe that ammonium manganese phosphate is soluble in ammonium chloride does not hold if there is an abundance of the soluble precipitating phosphate present. Further, our experience goes to show that the precipitate may be washed with perfect safety with pure water as well as with slightly ammoniacal water, or with ammoniacal water containing ammonium nitrate, if the filtration is performed rapidly and the precipitate is gathered in small space, as is the case when the phosphate is collected on asbestos in a perforated crucible. The finely granular precipitate which may be obtained by slow action of dilute ammonia added gradually to the hot solution of the manganese salt apparently includes a portion of unconverted phosphate which resists the replacement of the manganese by ammonium. On the other hand, the precipitate of flocky condition thrown down in the cold passes easily to the silky and crystalline condition when heated with the proper amount of ammonium salt and possesses a constitution approaching the ideal under such conditions. The conversion of the flocky manganous phosphate is so rapid that the precipitation may be carried on safely in glass vessels. If the ammonium chloride in the solution were to be included in the precipitate it would volatilise entirely during the ignition, leaving no trace unless, possibly, a portion of its chlorine were to combine with the manganese. Tests for chlorine in the residue of pyrophosphate resulted negatively—no more than a mere trace being found in any case, so that the contaminating effect of the ammonium chloride proves to be insignificant, and the responsibility for the increase in weight above the theory must apparently rest with the included microcosmic salt.

In the practical determination of manganese by the phosphate method of Dr. Gibbs, therefore, we advocate strongly the presence of large amounts of ammonium chloride. Good results may be obtained by the method of precipitation originally laid down by Dr. Gibbs, or by the modification proposed by Blair, if the ammonium salt is present in sufficient quantity. On the whole, trustworthy results are obtained most easily and surely, according to our experience, by following the method of the experiments of Table V. The slightly acid solution, containing in a volume of 200 c.m.^{3} (in platinum or glass) an amount of manganese not more than enough to make 0·4 grm. of the pyrophosphate, 20 grms. of ammonium chloride, and 5 to 10 c.m.^{3} of a cold saturated solution of microcosmic salt, is precipitated in the cold by the careful addition of dilute ammonia in only slight excess. The mixture is heated until the precipitate becomes silky and crystalline, the whole is allowed to stand and cool a half hour, the precipitate is collected upon asbestos in a perforated platinum crucible, washed (best with slightly ammoniacal water), dried at gentle heat, and ignited as usual. By this process determinations of the larger amounts of manganese—0·4 grm. of the pyrophosphate—approximate rather more closely to the theoretical values than do those of the smaller amounts—0·15 grm. In either case the average error should not exceed 0·0010 grm. in terms of manganese.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 7th, 1898.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of October has been 4·59 inches; as the average for the last thirty years is only 2·57 inches, we have an excess of 1·84 inches. This reduces the deficiency for the year to 6·38 inches, or 30·09 per cent.

Our bacteriological examinations of 257 samples have given the results recorded in the following table; we have also examined 55 other samples, from special wells, standpipes, &c., making a total of 312 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	1234
New River, filtered (mean of 26 samples) ..	22
Thames, unfiltered (mean of 26 samples) ..	8804
Thames water, from the clear water wells of five Thames-derived supplies (mean of 127 samples)	28
Ditto ditto .. .. highest	316
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	1719
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	13

The average daily flow of the Thames over Teddington Weir, for the present year to the end of the drought, is 550 million gallons, as compared with 826 million gallons, the

average daily flow for the same period during the ten preceding years. Thus there has been a deficiency of one-third in the average daily flow of the river since the beginning of the year to October 17th, when the drought ended.

The extraordinary drought—the most severe for at least 40 years—having ended, there are several matters which deserve consideration. The average bacteriological condition of the raw, unfiltered Thames and Lea waters during that period was exceptionally good, seeing that the bulk of the supply was spring water. The condition of the filtered water supplied to London was excellent, and in the case of the East London supply the quality was substantially the same as during similar seasons when the supply of water was ample.

The large rainfall which took place in October has had the effect of suddenly washing into the rivers organic matter accumulated on the water-shed during the three previous months, and as the reservoirs of the East London Company were almost empty at the end of September the Company was forced, in October, to use the Lea, without the advantage of the purification resulting from proper storage in the reservoirs. During this critical time we took extra pains to ascertain the character of the East End supply, and additional samples were regularly taken from various points in the district. It is highly satisfactory to report that, in spite of the severe strain thus thrown on their filtering appliances, the clear water supplied to East London has been, bacteriologically, better than it was during the months of August and September.

It has been shown over and over again in these reports that, as a matter of fact, the bacteriological quality of the London water supply does not depend on the use or rejection of flood water, but upon the proper regulation and the efficiency of the filtration. This has long been conducted, substantially, under the supervision of the official Water Examiner appointed under the provisions of the Metropolis Water Act, 1871. The direct use of water from the river during a prolonged flood, depending somewhat on the time of year, may result in the filtered supply containing in solution a little additional vegetable matter, thereby slightly adding to the brown colour, but in our experience during the last fifteen years we have seldom, if ever, known the colour of the London water supply, in its most peaty condition, to equal that of the average colour of Loch Katrine, Thirlmere, or the Welsh Lakes.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

The following are the abstracts of papers received during the vacation and published in the *Transactions*:—

101. "*The Vapour Pressures, Specific Volumes, and Critical Constants of Normal Heptane.*" By Sydney Young, D.Sc., F.R.S.

The critical constants of the specimen of normal heptane obtained by Dr. Thorpe from *Pinus sabiniana* are:—temperature, 266·9°; pressure, 20,415 m.m.; volume of a grm., 4·266 c.c.

A comparison of the ratios of the absolute temperatures (boiling-points) and volumes (liquid and saturated vapour) to the critical constants with those of normal pentane and normal hexane at "corresponding" pressures, shows that, whilst the deviations from constancy are small, the temperature ratios are certainly—and the volume ratios are probably—related to the molecular weights of the paraffins, but a full discussion of this relationship is reserved until the data for normal octane have been obtained.

102. "*Contributions to the Chemistry of Phenol Derivatives.*" By Raphael Meldola and Frederick Henry Streatfeild.

When phenol is brominated in acetic acid solution with one molecular proportion of bromine, and the product afterwards nitrated, a mixture of 4-bromo-2-nitrophenol and 2-bromo-4:6-dinitrophenol is always obtained (*Trans.*, 1896, lxix., 1326). In the present paper the authors show that the bromodinitrophenol is the result of the nitration of both the para- and ortho-bromophenols present in the crude product. The presence of orthobromophenol is proved by the formation of 2-bromo-4-nitrophenol, which the authors have succeeded in isolating from the mixture of nitro-derivatives. The formation of 2-bromo-4:6-dinitrophenol from parabromophenol is not due to "isomeric change" as ordinarily understood, since the first product of the nitration of 4-bromo-2-nitrophenol under the conditions of nitration employed is 4-bromo-2:6 dinitrophenol, and this undergoes isomeric change only when heated with bromine and water (Armstrong, *Trans.*, 1875, xxviii., 520), or nitric acid (Gordon, *Proc.*, 1891, vii., 64), or at ordinary temperatures when the solution in excess of fuming nitric acid is allowed to stand for about two hours. The statement of Hübner and Brenkin (*Ber.*, 1873, vi., 170), that when phenol is brominated in acetic acid and the solid (para) bromophenol frozen out a liquid isomeride in the mother-liquor remains, is thus confirmed. At the same time, the suspicion expressed by Armstrong (*loc. cit.*, 521), that pure parabromophenol gives some "bromo-α dinitrophenol" on nitration, is also confirmed.

The authors have also studied the products of the nitration of pure orthobromophenol. These are 2-bromo-4-nitrophenol (m. p. 112°) and 2-bromo-6-nitrophenol, a new modification (m. p. 67—68°), of which the silver, barium, potassium, and methyl salts are described.

On limited reduction, 4-bromo-2:6-dinitrophenol yields 4-bromo-2-nitro-6-aminophenol (m. p. 141—142°), from which the acetyl derivative (m. p. 161—162), the methyl ether (m. p. 81—82°), and 4-bromo-2:6-dinitraniline were prepared.

The following derivatives of guaiacol were also obtained:—4-bromo-2-nitroguaiacol (m. p. 103—104), 2-bromo-4-nitroguaiacol (m.p. 142°), and acetamidoguaiacol [OH:OMe:NHAc = 1:2:6], crystallising from water with $1H_2O$, which is lost at 100°.

103. "*Some Iodoso-compounds.*" By John McCrae, Ph.D.

In order to ascertain whether diortho-substituted phenylic iodides yield dichlorides and iodoso-derivatives, the behaviour of orthiododimetadibromotoluene and symmetrical tribromiodobenzene was investigated. The dichlorides were not obtained quite so easily as in the cases of simpler iodides, but this is due to the fact that the iodide dichlorides of these two compounds are more easily soluble in chloroform than the iodides themselves; consequently the dichlorides did not separate until some of the chloroform had evaporated. The dichloride, iodoso-, and iodoxy-derivatives of 5-nitro-2-iodotoluene were also prepared.

104. "*On Myrticolorin, the Yellow Dye Material of Eucalyptus Leaves.*" By Henry G. Smith.

Myrticolorin, $C_{27}H_{28}O_{16}$, exists in large quantity in the leaves of the "red stringy bark," *Eucalyptus macrorhyncha*, and is a new glucoside of quercetin occupying an intermediate position between osyritrin, $C_{27}H_{30}O_{17}$, obtained from the Cape sumach (A. G. Perkin, *Trans.*, 1897, lxxi., 1132), and Viola quercitrin, $C_{27}H_{26}O_{15}$, from the flowers of *Viola tricolor variensis*.

The sugar gave an osazone melting with slight decomposition at 180° when slowly heated, and at 190° with rapid decomposition when rapidly heated. As the osazone of galactose is indicated by these results, and as manna

containing sugars is not obtained from the group of Eucalypts to which *E. macrorhyncha* belongs, whilst the principal sugar of the members of the group which do exude manna is raffinose, the question becomes one of importance, and the sugar of myrticolorin will be further examined.

In colour, melting-point, reactions with reagents, and dyeing power, no differences could he detected between myrticolorin and osyritrin, a specimen of which had been forwarded by Mr. A. G. Perkin for comparison.

105. "*Chemical Properties of Concentrated Solutions of certain Salts.* Part II. *Double Potassium Succinates.*" By William Colebrook Reynolds.

The result of the addition of many metallic salts to a concentrated solution of potassium succinate resembles that obtained with a concentrated solution of potassium carbonate (*Trans.*, 1898, lxxiii., 262). Crystalline double succinates, more or less soluble in the solution, were obtained instead of the insoluble metallic succinates in the case of nickel, zinc, cobalt, lead, and calcium.

106. "*Additive Compounds of Organic Bases and Ethereal Salts of Unsaturated Acids.*" By S. Ruhemann and K. C. Browning.

The authors have found that the view expressed by Ruhemann and Hemmy (*Trans.*, 1897, lxxi., 334), with respect to the mode of formation of the compound regarded provisionally as triethylic anhydro-oxalaconitate is correct, as ethylic oxalacetate alone takes part in the reaction. Whilst endeavouring to determine the constitution of that substance, they have observed that piperidine forms additive compounds with ethereal salts of unsaturated acids. These distil in a vacuum without decomposition, have basic properties, and form hydrochlorides which are very soluble in water. The following additive compounds are described: — Ethylic piperidylsuccinate (b. p. 159° at 10 m.m.), ethylic piperidylpyrotartrate (b. p. 163—164° at 10 m.m.), ethylic piperidyltricarballylate (b. p. 201—202° at 10 m.m.), and ethylic piperidylcinnamate (b. p. 220—221° at 11 m.m.

107. "*Formation of Ethereal Salts of β-Ketonic Acids.*" By S. Ruhemann and K. C. Browning.

Adopting Michael's method for the formation of ethereal salts of β-ketonic acids by the combination of ethylic sodio-acetoacetate with the ethylic salts of unsaturated acids, the authors have prepared ethylic α-acetotricarballylate (b. p. 187—188° at 11 m.m.), ethylic acetoethyltricarballylate (b. p. 194 — 196° at 9 m.m.), ethylic α-benzoyltricarballylate (b. p. 244—245° at 10 m.m.), and ethylic α-acetobutanetetracarboxylate (b. p. 222—223° at 10 m.m.),

108. "*Disulphonic Acids of Toluene, of Ortho- and Para-toluidine, and of Ortho- and Para-chlorotoluene.* By William Palmer Wynne, D.Sc., F.R.S., and James Bruce, B.Sc.

The authors correct certain errors which occur in their previous communication (*Proc.*, 1895, xi., 153), and show that the para-toluidinedisulphonic acids obtained by Richter from the 1:4:3- and 1:4:2-para-toluidinesulphonic acids (*Annalen*, 1885, ccxxx., 314, 331) are the 1:4:3:5- and 1:4:2:5-derivatives respectively. They also show that the toluene disulphonic acid previously described as the 1:2:6-derivative is the 1:2:5 compound.

Paratoluidine-3:5- and 2:5-disulphonic acids, and orthotoluidine 3:5- and 4:5-disulphonic acids, together with the corresponding chloro-acids, are described, and the statements of Hasse (*Annalen*, 1885, ccxxx., 286) with respect to the bromotoluenedisulphonic and toluenedisulphonic acids derived from orthotoluidine-3:5-disulphonic acid are shown to be erroneous.

Parachlorotoluene-3- and -2-sulphonic acids, and orthochlorotoluene-4-sulphonic acid, together with the disulphonic acids derived from them by further sulphonation are described, and the conclusion is drawn that the mixture of monosulphonic acids obtained on sulphonating parachlorotoluene contains not more than 14 per cent of the 1:4:3-isomeride.

Incidentally, the list of six toluenedisulphonic acids given by Klason (*Ber.*, 1887, xx., 350) has been revised, and it is shown that only five of the six acids theoretically possible are known. Experiments are in progress with the object of obtaining the missing 1:2:3-isomeride.

109. "*Chlorine Derivatives of Pyridine.* Part II. *Interaction of Ammonia and Pentachloropyridine. Constitution of Glutazin.* By W. T. Sell, M.A., and F. W. Dootson, M.A.

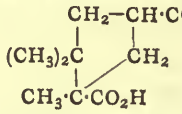
The authors describe the preparation from pentachloropyridine of γ-amidotetrachoropyridine, (presumably α-) amidotetrachloropyridine, diamidotrichloropyridine, and hydroxytetrachloropyridine. γ-Amidotetrachloropyridine is identical with the compound obtained by Stokes and Pechmann (*Ber.*, 1887, xx., 2655) from glutazin, and thus demonstrates the presence of an amido-group in the latter substance.

110. "*Mercury Acetamide.*" By M. O. Forster, Ph.D., B.Sc.

Mercury acetamide liberates nitrogen from hydroxylamine, hydroxylamine hydrochloride, hydrazine, hydrazine hydrochloride, and phenylhydrazin, being resolved by these substances into acetamide and mercury, which, in the case of the salts mentioned, are accompanied by calomel; the products from phenylhydrazin are aniline, benzene, and mercury diphenyl. Phenylhydroxylamine is converted into nitrosobenzene and azoxybenzene by the agency of mercury acetamide, which transforms hydrazobenzene into azobenzene. Nitrosophenylhydroxylamine, aniline, and diazoamidobenzene yield additive compounds with mercury acetamide.

111. "*Sulphocamphylic Acid and Isolauronolic Acid, with Remarks on the Constitution of Camphor and some of its Derivatives.*" By W. H. Perkin, jun.

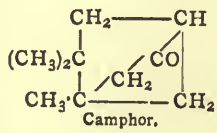
In this communication the author shows that the results which he and others have obtained in the investigation of isolauronolic acid can, apparently, be explained only on the assumption that camphoric acid has the formula—



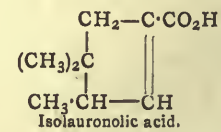
With the aid of this formula, the oxidation of isolauronolic acid, $C_9H_{14}O_2$, to isolauronic acid, $C_9H_{12}O_3$, and further to γ-acetyldimethylbutyric acid,—

$$CH_3{\cdot}CO{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

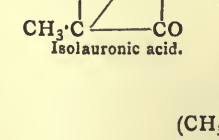
is readily understood. Assuming that the above constitution for camphoric acid is correct, the author deduces the following formulæ as probably representing the constitution of some of the more important members of the camphor group:—



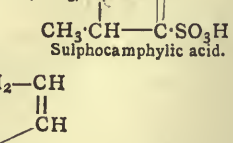
Camphor.



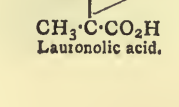
Isolauronolic acid.



Isolauronic acid.



Sulphocamphylic acid.



Lauronolic acid.

These formulæ are shown to explain the properties of the substances in a satisfactory manner.

112. "*Researches on the Terpenes.* VIII. *On Carvenol: its Reactions and Products.*" By J. E. Marsh and A. Hartridge.

Carvenol, the product of the action of strong sulphuric acid on chlorocamphene, and previously described as hydroxycamphene or camphenol (*Trans.*, 1897, lxxi., 290), has been further examined. It has been found to yield chlorocymene [Me : Cl : $P_1\beta$ = 1 : 2 : 4] by the action of phosphorus pentachloride, and paracymene by the action of benzoic chloride. It is reduced by sodium in alcoholic solution, forming the secondary alcohol *carvanol*, $C_{10}H_{20}O$, which is hexahydrocarvacrol. This latter compound yields, on oxidation, the saturated ketone *carvanone*, $C_{10}H_{18}O$.

The production from camphor of cymene and chlorocymene by comparatively simple reactions, and also of reduced cymene derivatives, brings into prominence the close relationship which must exist between camphor and cymene. Not only do formulæ which fail to express this relationship in the arrangement of the carbon atoms lose the chief support on which any formula for camphor must rely, but, further, in view of the production of chlorocamphene, a saturated compound, no formula can be admitted which leads to the representation of camphene and chlorocamphene as unsaturated compounds.

113. "*Optically Active Alkyloxypropionic Acids.*" By Thomas Purdie, F.R.S., and G. Druce Lander, B.Sc.

As the product of the action of isopropylic iodide on inactive silver lactate contains a considerable quantity of isopropylic isopropoxypropionate (*Trans.*, 1898, lxxiii., 296) the authors concluded that the abnormally high rotation of the active ethereal lactates prepared by the silver salt method (*Trans.*, 1895, lxvii., 916; 1896, lxix., 830) was due to their contamination with small quantities of active ethereal alkyloxypropionates. If this conclusion is correct, the alkyloxypropionic acids must be substances of very high optical activity. With the view of verifying this, the active *a*-methoxy, ethoxy, and propoxy-propionic acids have been prepared.

As complete racemisation occurs during the action of sodium ethylate on active ethylic chloro- and bromopropionates (*Trans.*, 1896, lxix., 819), the active alkyloxyacids were prepared by the re-solution of the inactive acids with alkaloids. The re-solution of ethoxypropionic acid was carried out with cinchonidine, and more completely with morphine, the salt of the dextro-acid being in both cases the less soluble. The methoxy- and propoxyacids were also resolved with both alkaloids, but the resolution with cinchonidine was far from complete. In the case of the methoxy-acid, both alkaloids precipitate first the lævo-acid; in the case of the propoxy-acid, the cinchonidine salt of the lævo- snd morphine salt of the dextro-acid are first deposited. The authors point out that the results of their experiments are not in harmony with the theory of Winther (*Ber.*, 1895, xxviii., 3000).

Polarimetric observations were made on the *l*-methoxy-, *d*-ethoxy-, and *d* propoxy-acids, and on their sodium and calcium salts, also on barium and silver *d*-ethoxypropionates. The substitution of the alcoholic hydrogen of the lactates by an alkyl-group produces, as was expected, a great increase of optical activity. Thus the molecular rotation of the alkaline lactates in dilute aqueous solution is 14·5°, while that of sodium ethoxypropionate is 68·77°. Increase in the weight of the introduced alkyl group produces a very much smaller but still distinct rise of molecular rotation. The rotations of the salts increase with dilution, and in general conform to the law of Oudemans and Landolt; those of the acids diminish. The changes of rotation with varying concentration are, as might be expected from the disappearance of the hydroxyl group, of a more normal kind than in the case of lactic acid and the lactates, but the authors conclude that even in the case of the alkyloxy-acids, the rotation is influenced by other factors connected with the solvent besides electrolytic dissociation.

114. "*The Optical Activity of Gallotannic Acid.*" By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.

The authors have examined a number of commercial "pure" gallotannic acids, and find that, whilst they varied in optical activity from $[\alpha]_D + 11°$ to $[\alpha]_D + 74·2°$, they all contain from 50 to 75 per cent of a uniform gallo-tannic acid possessing an optical activity of approximately $[\alpha]_D + 75°$. The authors ascribe this great difference to the fact that the commercial substances contain varying quantities of gallic acid, which is inactive, and mineral matter, which possesses a great influence on rotatory power. Acetyl derivatives and quinine salts prepared from the commercial samples are respectively identical in optical activity among themselves and with the products obtained from the homogeneous substance isolated by the author's method.

115. "*The Influences Modifying the Specific Rotatory Power of Gallotannic Acid.*" By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.

The authors have examined the modifying influence of—(*a*) concentration, (*b*) nature of the solvent, and (*c*) optically inactive substances, on the specific rotation of gallotannic acid. The material used for these experiments was the homogeneous product obtained by methods described in the preceding paper. The results were as follows:—

(*a*). *Concentration.*— In aqueous solutions containing not more than 1 per cent, the rotation is constant at $[\alpha]_D$ 15 +75·2°. From 1 to 10 per cent, the rotation decreases gradually to $[\alpha]_D$ 15 +66·1°.

(*b*). *Nature of the Solvent.*— The optical activity of gallotannic acid depends to a very marked extent on the nature of the solvent. Thus, the original specific rotation $[\alpha]_D$ 15 +75·2° (for water) is reduced to ± 0° for a mixture of acetone and carbon tetrachloride. Alcohol, ethylic acetate, &c., and mixtures of acetone with ether, &c., have a powerful depressing action, and the gross effect produced is greater in the case of gallotannic acid than in that of any other substance hitherto examined.

(*c*). *Influence of Optically Inactive Substances.*— 1. *Acids:* Mineral acids have no influence. Acetic acid has a depressing effect, but this is probably due to partial acetylation. Gallic acid has no influence. 2. *Ammonia:* A few drops added to a 1 per cent solution produce total inactivity. 3. *Salts:* Salts, such as sodium tungstate, sodium, potassium, ammonium, and lithium biborates and chlorides, sodium and potassium bicarbonates, and zinc acetate, exercise a very marked influence on the rotation of gallotannic acid. In the majority of cases, the addition of increasing amounts of salt produces a decrease in the specific rotation until a minimum is attained, the further addition of salt causing a gradual rise. The molecular rotations of the mixtures at the minima are approximately constant and equal to the molecular rotation of gallotannic acid alone.

116. "*The Non-resolution of Racemic Tetrahydropapaverine by Tartaric Acid.*" By William Jackson Pope and Stanley John Peachey.

Prior to the publication of Goldschmiedt's paper (*Monats.*, 1898, xix., 321), the authors had prepared the dextrotartrate of racemic tetrahydropapaverine in the course of their work on the re-solution of the base into its optically active components (*Proc.*, 1898, xiv., 122). The salt has the composition assigned to it by Goldschmiedt, and belongs to the monosymmetric system; $a : b : c$ = 1·1464 : 1 : 0·7932; β = 82° 30'. Its molecular rotation was found to be $[M]_D = +63·44°$, a value agreeing with those obtained for the metallic tartrates in dilute aqueous solution, namely, 58·1 to 64·6 (Landolt, *Ber.*, 1873, vi., 1077).

Ladenburg has described as "hemiracemic," salts in which either the acid or the base is racemic whilst the other constituent is optically active, and has examined two salts of the kind, namely, quinine racemic pyrotartrate

(*Ber.*, 1898, xxxi., 524, 937) and strychnine racemate (*Ber.*, 1898, xxxi., 1969). Racemic tetrahydropapaverine dextrotartrate is thus the first case of the kind in which a racemic base is combined with an optically active acid.

PHYSICAL SOCIETY.

Ordinary Meeting, November 11th, 1898.

Mr. Shelford Bidwell, F.R.S., President, in the Chair.

The discussion on Mr. Albert Campbell's paper on "*The Magnetic Fluxes in Meters and other Electrical Instruments*" was resumed.

Prof. Ayrton said he wished to offer some remarks on behalf of Mr. Mather and himself. The paper would perhaps have received more adequate discussion at the Institution of Electrical Engineers, for it was chiefly of a technical character. The importance of neutralising the effect of leads when using instruments with very weak fields, such as Siemens's electro-dynamometer, should be emphasised. In instruments of the Kelvin-balance type, where two opposed coils carry two opposed currents, the field spreads at the edges; the true "working" flux is not that directly between the coils. Mr. Campbell would have done better if he had used a long search-coil wound round one of the swinging coils, forming part of a vertical cylinder. It would have been well also to have supplied some experimental proof that the astatic arrangement of the swinging coils of the Kelvin balance makes the instrument independent of the earth's field. The effect of the earth's field is of the order 0·2, so that with instruments of the Weston type, with a field of the order 1000, it was sometimes assumed, erroneously, that the readings were practically independent of the earth's H. Prof. Ayrton's own tests showed that by turning a Weston voltmeter towards different points of the compass, the errors in a particular case were far greater than might be predicted from the above ratio; the induction in the voltmeter pole-space, due to the earth's field, was much higher than 0·2; the earth's field was exaggerated by the iron pole-pieces; it was not necessary to suppose that the magnetism of the permanent magnet caused the variation. The error observed was about 0·2 per cent in a horizontal field, and 0·8 per cent when the field of the voltmeter was parallel to the earth's induction. Here the induction in the gap was 1200, and H=0·2. In tests relating to the Ayrton and Perry magnifying-spring voltmeter, it was more important to know the B in the air-space *near* the iron than the B *within* the iron. Eddy currents might account for the extraordinary results obtained in the Shallenberger meter.

Mr. J. H. Reeves described a method he had adopted for measuring the effect of stray fields upon ammeters and voltmeters. The instrument to be tested is first mounted on a stand, and is brought under the influence of a large coil carrying a current. In this way fields of known magnitude can be superimposed on the working field throughout the range of the instrument, and the change of deflection due to them can be observed. From these known values the working field can be deduced. For let the current in the solenoid of the instrument at any moment be A ampères, producing a corresponding unknown working field of magnetic force X. Then X is proportional to the solenoid current, as measured by the indications of the instrument. If a magnetic force x is superimposed on X, then x is measured by x/X of A. If x is known, the working field X can be calculated from the change of deflection produced by the superposition. With Eversheds ammeters the field measured in this way was in one instrument 200, and in another 226; or about one-third of Mr. Campbell's figure (700) for the Eversheds ammeter. Mr. Campbell's value of B did not represent the working field, but the field at the end of one of the fixed pieces of iron.

Mr. Campbell, in reply, said he thought the theory of electrical instruments to be well within the limits of Physics, and he had for that reason presented the paper to the Physical Society. The position chosen for the search coil in the Kelvin-balance tests may not have corresponded to the working flux, but it was near to the right position, and he had carefully specified the position chosen. His results as regards the Weston instrument differed from those of Prof. Ayrton; the errors he had observed for the particular ammeter used were under 0·1 per cent. The earth's field probably produced an effect different for different Weston instruments, according to the degree of saturation of the permanent magnet. In Mr. Campbell's tests the Weston instrument did not have an iron case.

A paper by Prof. W. B. Morton, on "*The Propagation of Damped Electrical Oscillations along Parallel Wires*," was then read by Prof. J. D. Everett.

In a paper published in the *Phil. Mag.* for September, 1898, Dr. E. H. Barton compared the attenuation of electrical waves in their passage along parallel wires, as experimentally determined by him, with the formula given by Mr. Heaviside in his theory of long waves. He finds close agreement as regards the effect of a terminal resistance, but large discrepancy in the case of the attenuation-constant. Prof. Morton now investigates how far the results should be modified when it is supposed, as under actual conditions, that the oscillations propagated from the origin are damped, and that the circuit is not balanced, as in the ideal case of distortionless transmission. He finds (1) that the velocity of propagation is increased, while (2) the attenuation is increased, and (3) with infinite resistance between the ends of the wires, the waves are, as before, reflected completely with phase unchanged. As the resistance is diminished the amplitude of the reflected waves is decreased, and a phase-difference is introduced. For a certain value of the resistance the reflected amplitude is a minimum, and the phase-difference is $\pi/2$. When the resistance is zero, there is again complete reflection, with phase-difference π; *i.e.*, the waves are reversed. The result is that the reflection-factor for amplitude *seems* to pass continuously from (+1) to (−1) *without* passing through zero. Using the numbers given by Dr. Barton it is found that the corrections to the simple theory are extremely small, so that in actual cases the damping may be ignored, and the circuit may be regarded as distortionless.

Mr. Oliver Heaviside (abstract of communication).—Mr. Heaviside, using his own notation, exhibits mathematically the connection between the case investigated by Mr. Morton, of a wave-train arising from a damped source, and the standard case of an undamped source. The cause of the attenuating coefficient coming out twice as great in Dr. Barton's experimental conditions as when the resistance is calculated by Lord Rayleigh's formula, is attributed to lack of correspondence between the experimental conditions and those of the ideal theory. For—(1) The external resistance, of unknown amount, is ignored. (2) It is not certainly to be expected that the formula in question is true for millions of vibrations per second. It may, however, be concluded from the experiments that the theory furnishes an approximation to the real resistance. (3) The magnetic vibrations to which the wires are subjected are not long-continued and undamped, as assumed by the formula. When a wave train passes any point on a wire its surface is subjected to an impulsion vibration lasting only a very minute fraction of a second; a vibration, moreover, which is very rapidly damped. So there is no definite resistance, and the resistance is greater than according to Lord Rayleigh's formula. (4) Perhaps, also, the terminal reflections involved in Dr. Barton's calculations may introduce error.

The President proposed votes of thanks to the author, and the meeting was adjourned until Nov. 25th.

NOTICES OF BOOKS.

Twenty-second Annual Report of Her Majesty's Inspectors of Explosives. Being their Annual Report for the Year 1897. London: Eyre and Spottiswoode. Edinburgh and Glasgow: John Menzies and Co. Dublin: Hodges, Figgis, and Co. 1898. Pp. 208.

THE report of Her Majesty's Inspectors of Explosives shows in a very emphatic manner what minute but rigorous precautions are taken to guard against accidents in the manufacture and handling of the enormous and ever-growing trade in high explosives. Accidents accompanied by death or maiming are comparatively rare, thanks to the vigilance of the inspectors.

There has been no further modification in the law during the year; but an Order in Council (No. 17) has been made under Section 104 of the Act placing acetylene when in the liquid state, or subject to a certain pressure, on the list of explosives within the meaning of the Act.

The number of factories has decreased by one, but three new ones have been added since 1896, while ten applications for new licences are still under consideration. The four extinct factories were either practically not in use or have been superseded by new ones. Every factory and magazine has been visited at least once, and many of them twice, during the year.

The number of deaths from accident has been only nine, and although above the ten years' average (5·2), it is, as we pointed out above, relatively inconsiderable.

Eight new explosives have been added to the authorised list, full definitions of which will be found in Appendix D (1). Out of 321 samples of explosives examined during the year, only 26 were rejected.

There has, we are glad to see, been no falling off in the general improvement referred to in the last report. A very high standard of excellence was reached soon after the passing of the Act in 1871, and this has been fully maintained during the past year; in fact, in only one case was it found necessary to take proceedings, and in only three cases explosives were placed under seizure.

The total number of magazines is now 390, being an increase of six over last year, and it is satisfactory to note that there has been no case of unlawful entry into either a magazine or factory during the year, neither has there been any case of fire or explosion in any of the 390 magazines during the same period.

There is a decrease in the quantity of foreign nitroglycerin compounds imported during the year. In 1896 the amount imported was 1,259,200 lbs., and in 1897 it had fallen to 1,153,550 lbs. The amount of carbonite has fallen off, and gelatin dynamite again heads the list.

In the special section on accidents are to be found tables giving not only the few which have occurred at factories, but also many others in different parts of the country, due to carelessness or else unexplained. We note that in the last ten years there have been only 14 deaths due to explosions of gunpowder. Following the practice of former years, a brief account of the more interesting foreign explosions is also given. On September the 8th some dynamite exploded at the George Goch mine, Johannesburg, killing 8 natives and wounding 12 others; and in April two cases of blasting gelatin exploded in the 1250 foot level of the Langlaagte Deep, Johannesburg, by which 8 white men and 26 natives lost their lives. The explosion shook the whole of the upper levels. At San Salvador, in America, a dynamite explosion occurred by which two blocks of buildings were destroyed and a number of persons killed. There were also several serious explosions of fireworks reported by which many people were killed and injured in different parts of America. At Cumpas, in Mexico, 3 tons of blasting powder blew up, killing 20 people and injuring others, while nearly every building in the town was injured. A terrible explosion took place at Rustchuk on the 6th of August, by which 200 people were killed. Several million old army cartridges were being emptied in one large shed in which over 300 persons were employed; it is supposed that a cartridge was dropped, but the wonder is that anyone escaped. There are many others of more or less magnitude in the list, but it would be tedious and unprofitable to go through them. Thanks, however, to the thorough and excellent system of storage, isolation, and inspection adopted in England, we are practically free from such terrible catastrophies we so often hear of from abroad.

Pharmaceutical Formulas: a Book of Useful Recipes for the Drug Trade. Second Edition. By PETER MACEWAN, F.C.S. London: Office of the *Chemist and Druggist.* 1898. Pp. 664.

THE rapidity with which this edition has followed the first, which was published only one month previously, shows that there was a great demand for such a book. The task of collecting and collating the very large number of formulas has been a formidable one. A large proportion of them had to be proved, and the results of these provings are partly embodied in the book. The formulas have been taken principally from *The Chemist and Druggist* and "The Chemist's and Druggist's Diaries," and include such various matters as toilet preparations, hair washes, dentifrices, beverages, antiseptics, disinfectants, inks, varnishes, medicinal compounds, &c.

The customary signs employed in prescriptions are as a rule used in the formulas, and the British rule "solids by weight, liquids by measure," applies throughout unless otherwise stated. An Addenda informs the reader that, owing to the publication of the British Pharmacopœia, 1898, a certain number of formulas (the list is given in full) should be compared with those in the Pharmacopœia and the changes noted.

There is no doubt but that this book will be of great value to druggists and pharmaceutical chemists, and will cause them a great saving of time. We are glad to see that there is an excellent index of 25 pages, enabling any formula to be found almost immediately.

Elementary Physics, Practical and Theoretical. First Year's Course. By JOHN J. KERR, M.A. London: Blackie and Sons, Lim. 1898. Pp. 140.

THIS book is divided into two principal parts, viz., Laboratory Work, from page 1 to page 63; and Classroom or Theoretical Work, from page 64 to 140. These chapters, seventeen of each, correspond and should be read together. They begin with the measurement of length, the vernier and screw gauge are then described, after which we have the methods of measurement of area, volume, mass, time, and force, accompanied by descriptions of, and the manner of using, the spring balance, the beam balance, and the pendulum. The next few chapters deal with the parallelogram of forces, the inclined plane, movements, centre of gravity, &c., and the final ones explain the principle of Archimedes, the pressure due to liquid columns, the hydrometer, and Boyle's law. It is essentially a book for beginners, and is well arranged; everything is clearly and thoroughly explained both in the practical and theoretical parts, and should be of great help to young students.

The Rare Earths; their Mineralogy, Properties, and Analysis. ("Les Terres Rares; Minéralogie, Propriétés, Analyse"). By P. TRUCHOT. Paris: Georges Carré and C. Naud. 315 pages. Price 5 francs.

THIS work puts on record our present knowledge of the physical and chemical properties of the rare earths. The application of some of the earths of this group to the purposes of lighting have brought them into notice, and have given rise to a large amount of chemical literature. The work is divided into three parts.

1. *The Mineralogical Part* contains a valuable table of all the rare earth minerals; a detailed study of the principal minerals, especially the monazite sands, now almost exclusively employed in the manufacture of incandescent mantles; and a review of the geographical distribution of the chief deposits of these minerals, illustrated with maps.

2. *The General Part* contains a description of the rare elements and their organic and inorganic salts.

3. *The Analytical Part* comprises much that is known in France on the different methods of fractionation and separation, the analytical characters of the different rare earths, and the methods of analysis of commercial products, such as nitrate of thoria, precipitated thoria, monazite sands, incandescent mantles, &c.

This book will be useful to all who take an interest in the chemistry of the rare earths or who are engaged in the development of the important industries to which they have largely contributed. At the same time it has the great faults of so many otherwise excellent French books; it has no index, and it is written from a purely French point of view, little or no mention being made of the work done by Englishmen on the fractionation of the rare earths and in so many other directions.

A History of Chemistry from the Earliest Times to the Present Day; being also an Introduction to the Study of the Science. By ERNST VON MEYER, Ph.D., Professor of Chemistry in the Technical High School, Dresden. Translated, with the Author's Sanction, by GEORGE MCGOWAN, Ph.D. Second English Edition, translated from the Second German Edition, with numerous Additions and Alterations. London: Macmillan and Co., Lim. New York: The Macmillan Company. 1898.

IT is a great satisfaction to find that we have already a translation of the second edition of this well known and interesting work. Since the first edition, in 1891, many valuable sources of information have become available and have enabled the author to add much new matter in the earlier chapters of the book, while the many great advances that have been made in chemistry since that date have been followed up and included. Although professedly a translation of the second German edition of 1895, it has been brought quite up to date by additions both by the author and the translator with the author's sanction and approval. It has thus been possible even to include an account of the recent researches on the complex nature of the atmosphere by Rayleigh, Ramsay, and others.

We have little doubt that the appreciation that has been shown by English readers for the first edition will be extended also to this.

CORRESPONDENCE.

ESTIMATION OF SULPHUR IN COALS, COKES, AND ORES.

To the Editor of the Chemical News.

SIR,—Objection has been taken to our method of estimating sulphur (roasting with sodium carbonate, solution in water, filtering, acidulating filtrate with HCl, and precipitating by barium chloride, *vide Journ. Soc. Chem. Ind.*, March 29, 1886; *Journ. Iron and Steel Inst.*, 1896, No. 2) on the ground that silica from the ash, or gangue, entering into solution will be precipitated together with the barium sulphate. To our minds, this objection was met by the close agreement between the results obtained by our method and by the aqua regia method in the analysis of iron ores; but to put the matter to the test, we have examined the precipitates of $BaSO_4$ in varying experiments and have failed to detect the presence of silica in a single instance.

We find that some silica is dissolved by the water, but when the heat has not been so intense as partially to fuse the mixture, the amount dissolved is only small. But whether small or large, the barium sulphate is precipitated free from silica.—We are, &c.

R. W. ATKINSON.
ALEX. J. ATKINSON.

Laboratory and Assay Office,
14, Loudoun Square, Cardiff, Nov. 11, 1898.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 2, July 11, 1898.

Decomposition of Nitric Acid by Heat at Low Temperatures.—M. Berthelot.—When nitric acid was sealed up in a tube from which the air had been pumped out, and left in darkness for two months, no gas was formed if the tube was kept at the ordinary temperature of the laboratory; when kept in darkness at 100° it slowly decomposed, forming peroxide of nitrogen, oxygen, and water:—$2HNO_3 = 2NO_2 + O + H_2O$. The decomposition remained incomplete and could never become total owing to the formation of water. This water forms hydrates of nitric acid, which are much more stable than the pure acid. A limit was reached, and this was determined for a low temperature. If there is an inverse reaction produced at all in the cold it is excessively slow.

The Form of Oxidation of Cobalt Salts in Alkaline Solution.—André Job.—When a solution of a salt of cobalt is added drop by drop to a solution of bicarbonate of potassium a clear rose-coloured liquid is produced. A small quantity of peroxide of hydrogen or bromine water added to this turns the colour to green. Many attempts have been made to separate and analyse the green compound. The author obtains satisfactory results by employing ferrous solutions, which when added to the green cobalt solution change the green colour to rose. A known quantity of cobalt is peroxidised, and to it is added a known quantity of ferrous pyrophosphate; the excess of the latter is estimated by iodine. The numbers found agree with the oxidation formula, $2CoO + O = Co_2O_3$. The chief difficulty is to insure the complete peroxidation of the cobalt: to do this a large excess of hydrogen peroxide is added to the alkaline cobalt salt and left for several days. From this reaction a rapid and easy method of estimating cobalt in the presence of nickel and iron may be deduced; for nickel is not oxidised under these conditions, and ferric salts are not reduced by ferrous pyrophosphate.

Mixed Carbonic Esters of Phenols and Alcohols.—P. Cazeneuve and A. Morel.—By means of the general method of preparing mixed carbonic esters of the fatty and aromatic series, described by the authors in the preceding issue, mixed carbonates have been prepared of ordinary phenol and methyl, ethyl propyl, isopropyl, isobutyl, isoamyl, and allyl alcohols respectively. These esters have all been obtained by boiling phenyl carbonate with the different alcohols in presence of pyridine or urea. A description of their preparation and properties is given. It is remarked that the series thus obtained presents anomalies in certain physical properties which are unexplained at present. The boiling-points do not increase with the molecular weights, which, however, is the rule for esters of the same homologous series. With these mixed carbonic esters the boiling-point varies slightly for the different esters, under reduced as well as under normal pres-

sure, being about 220° at normal pressure and about 120° at a pressure of 30 m.m. Again, the density at zero of these esters, instead of increasing decreases from phenyl-methyl carbonate to phenyl-methyl-amyl carbonate.

Action of Heat on the Double Nitrites of the Metals of the Platinum Group. Rhodium Compounds.—A. Joly and E. Leidié.—The double nitrites which rhodium forms with potassium, sodium, and barium decompose under the influence of heat, giving salts comparable with those of ruthenium and iridium. The decomposition starts at 360°, but is quickest at 440°. The analysis of the decomposition products at this temperature shows the existence of RhO_2, which had been suspected by Claus, who hesitated whether to give it the formula RhO_2 or $RhO.RhO_3$. The decomposition reaction is probably represented by one of the two equations :—

$$3[Rh_2(NO_2)_{12}K_6] = = (6RhO_2K_2O)+6NO_2K+10NO_3K+3N+17NO,$$

or—

$$3[Rh_2(NO_2)_{12}K_6] = = (6RhO_2K_2O)+4NO_2K+12NO_3K+5N+15NO.$$

The Yttria Earths found in Monazite Sands.—G. Urbain.—Already inserted in full.

Bromination by means of Aluminium Bromide in the Fatty Series.—A. Mouneyrat.—In a previous paper the author has described the power of aluminium chloride to produce compounds containing double bonds with chlorhydrocarbons of the fatty series. He now finds that aluminium bromide has a similar effect upon brominated hydrocarbons. The following proof is given :—Anhydrous ethylene dibromide ($CH_2Br.CH_2Br$) is heated to 100—110° over a paraffin bath with anhydrous $AlBr_3$. Hydrobromic acid is copiously evolved and a gas which proves to be acetylene. The reaction probably occurs thus :—

$$(1)\ CH_2Br-CH_2Br+2AlBr_3 = = AlBr_2-CHBr-CHBr-AlBr_2+2HBr.$$

$$(2)\ AlBr_2-CHBr-CHBr-AlBr_2 = 2AlBr_3+CH\equiv CH.$$

The supposition now is that bromination can be effected by means of aluminium bromide. The brominating action of $AlBr_3$ upon ethyl bromide ($CH_3—CH_2Br$) was investigated. A solution of $AlBr_3$ in anhydrous bromine was used, and the compounds ethylene dibromide ($CH_2Br—CH_2Br$), acetylene tetrabromide ($CHBr_2—CHBr_2$), and hexabromethane ($CBr_3—CBr_3$) successively obtained. The formation of the latter compound is explained by the following equations :—

$$(1)\ CHBr_2-CHBr_2+2AlBr_3 = =AlBr_2-CBr_2-CBr_2-AlBr_2+2HBr.$$

$$(2)\ AlBr_2-CBr_2-CBr_2-AlBr_2+4Br = =CBr_3-CBr_3+2AlBr_3.$$

Hence we have a simple method of replacing in successive stages all the hydrogen atoms of ethane by bromine.

Action of Chlorides of Tetrazodiphenyl, Tetrazo-di-ortho-tolyl, Tetrazo-di-ortho-anisyl on the Cyanacetates of Methyl and Ethyl.—G. Favrel.—Not suitable for abstraction.

Rate of Saponification of the Esters of Phosphoric Acid.—J. Cavalier.—In order to compare, from the point of view of stability, the three phosphoric esters of any one alcohol, their rates of saponification by water are measured, the conditions of temperature and concentration being the same for each. On warming an aqueous solution of a neutral phosphoric ester, R_3PO_4, a mixture is obtained of the original ester and the three acids HR_2PO_4, H_2RPO_4, and H_3PO_4. Curves can be plotted representing, as a function of the time, the quantities of the different acids produced by decomposition of one molecule of the neutral ester, and the rates of decomposition of the three esters calculated. Results are given of a study of the three methyl esters and ethyl esters, and the two acid allyl esters. The methyl esters decompose more rapidly than the corresponding ethyl esters.

Journal de Pharmacie et de Chimie, vol. vii., No. 11.

The Estimation of Theobromine.—M. François.—The reactions of theobromine, like those of caffein based on oxidation, being difficult to recognise, the author gives two or three tests, with minute instructions as to their proper carrying out, and also the quantities to use. The test for purity is based on the very slight solubility of theobromine in strong alcohol, the most probable adulterant being caffein; the author has calculated the exact degree of solubility of both these substances in alcohol at 95 per cent, at a temperature of 21°. In testing for identity he dissolves 0·1 grm. of theobromine in a warm mixture of 1 part of nitric acid to 2 parts of water, then adds 10 c.c. of nitrate of silver at 10 per cent. A cloudiness is caused; the solution must be heated until it is clear on cooling; colourless needles are deposited. Another method is to use hydrochloric acid, and then add 10 c.c. of saturated bromine water; after heating to drive off the excess of bromine, the flask and its contents must be brought up to their original weight with distilled water. The cooled liquid stains the skin red. In determining the relative solubilities of theobromine and caffein the following constants were found :—10 c.c. of alcohol at 95°, saturated with theobromine at a temperature of 21°, contained 0·0045 grm. in solution, and under the same conditions 0·0930 grm. of caffein was contained in solution: from these data it is easy to calculate the amount of adulteration by caffein.

Note on Croton Oil.—M. Javillier.—Croton oil prepared by simple pressure, by lixiviation with ether at 0·758, or by double digestion at 75° in alcohol at 95° has different appearances, and gives different results on analysis, and also different returns; the first gave 12·5 per cent, the second 38 per cent, and the third 12 per cent. If 1 volume of the first oil be heated with 2 volumes of absolute alcohol, there is complete solution at 75°, but on cooling 0·8 per cent in volume of the oil separates; the second oil acts in the same manner, while the third is entirely soluble even in the cold. The first two oils congeal at −7° and the third at −8°, but they all commence to thicken before reaching zero. The index of iodine absorbed by these oils for 100 c.c. of each is—No. 1=109, No. 2=108, No. 3=91·2. Commercial oil generally has an index equal to 102. The index of saponification was found to be—No. 1=192·9, No. 2=194·5, No. 3=260·6, and commercial oil 205·6. The index of acidity was—No. 1=27·3, No. 2=30·9, No. 3=60·1. To sum up, it appears that the oil extracted by alcohol (No. 3) differs considerably from the other two, which are almost identical.

On the Acid Phosphoglycerates.—MM. Adrian and Trillat.—When we add to an aqueous solution of a glycerophosphate of baryta a little dilute sulphuric acid, a sulphate of baryta is formed, while the liquid remains neutral to heliantine; the precipitate continues to form until there is just an excess of acid. This reaction does not give free phosphoglyceric acid, but an acid salt; if this salt is treated with a soluble sulphate a double decomposition takes place. These two reactions show that it is possible to obtain acid glycerophosphates by two methods: —1st, by the decomposition of a neutral glycerophosphate by sulphuric acid; and 2nd, by double decomposition between an acid glycerophosphate and a soluble sulphate. The preparation of the acid salts of barium, zinc, and magnesia are then described, and the results of their analyses given. When an acid glycerophosphate is dried at 130° it appears to be anhydrous, but when powdered it is extremely hygrometric. The principal difference between these last and the neutral salts is their great solubility in cold water, as well as in water to which alcohol has been added. They are not sensibly decomposed by heat; they are distinguished from the neutral and acid phosphates by the same reactions as the neutral glycerophosphates; acetate of lead gives a white precipitate soluble in acetic acid; but neither molybdate of ammonia, acetate of uranium, nitrate of silver, or ferric chloride, give any precipitate at all.

MISCELLANEOUS.

The Countess of Warwick's Secondary and Technical School at Bigods, Dunmow, Essex.—We are pleased to learn, by the report of an Address delivered at the above Institution by Professor Raphael Meldola, F.R.S., that an attempt is being made to introduce scientific training into the rural districts. The wisdom of such a movement must be apparent to every one, and we can heartily commend the philanthropy and foresight of the lady to whom this first experiment is due. That a need exists in this direction is at last becoming recognised, and we hope that the experiment in Essex may meet with all the success it deserves, and lead to similar movements in other districts. No doubt difficulties will be met with at first, and possibly a good deal of indifference and want of appreciation from the very class whom it is desired to benefit; but difficulties can be overcome, and those who have the cause at heart will look rather to future results than present appreciation. We should not wonder if it is found that the *material* turns out to be of even better quality than the authors of the movement expect, for we cannot forget that among our greatest men there are many whose early years were spent far from the great centres of learning, and there are unquestionably many instances where true talent has either lain dormant or has developed abnormally for want of a little scientific training. We are really glad to find at least one attempt to replace by systematic scientific education the occasional spasmodic "lecture," that in many instances only tends to "amaze the unlearned," and we shall watch with interest the development of the movement.

Action of Arseniuretted Hydrogen on Mercuric Chloride.—A. Partheil and E. Amort.—When arseniuretted hydrogen is passed into an acoholic solution of mercuric chloride, a yellow precipitate is formed of composition $AsH(HgCl)_2$, the reaction being represented by he equation—

$$2HgCl_2 + AsH_3 = 2HCl + AsH.(HgCl)_2.$$

On continuing to pass AsH_3 into the solution the precipitate takes a brown colour, and its composition alters to—

$$AsHg_2Cl + HgCl_2AsH_3 + 3HgCl_2 = 3HCl + AsHg_3Cl_3.$$

The author performs a series of experiments to try to prepare the unknown substance AsH_2HgCl, but without success. However, when AsH_3 is continued to be passed into the alcoholic solution, the brown precipitate is blackened, the substance As_2Hg_3 being formed.—

$$As(HgCl)_3 + AsH_3 = 3HCl + As_2Hg_3.$$

—*Ber. der Deutsch. Chem. Gesellschaft*, 1898, No. 6.

MEETINGS FOR THE WEEK.

Monday, 21st.—Society of Arts, 8, (Cantor Lectures). "Acetylene," by Prof. Vivian B. Lewes.

Wednesday, 23rd.—Society of Arts, 8. "Long Distance Transmission of Electric Power," by Prof. George Forbes, F.R.S.

Friday, 25th.—Physical, 5. "Properties of Liquid Mixtures," by R. A. Lehfeldt. "Certain Diffraction Fringes as applied to Micrometric Observations," by L. N. G. Filon.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2035.

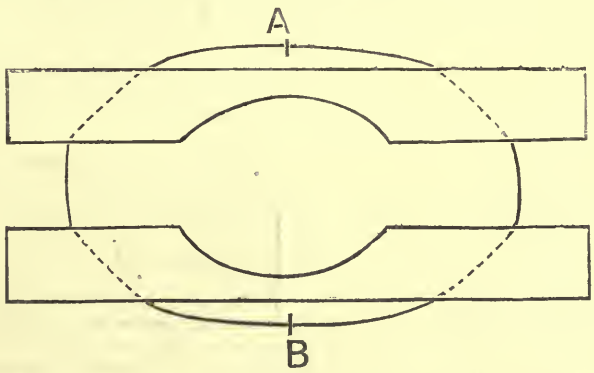
LABORATORY NOTES.

By HORACE JERVIS.

A New Clip.

The accompanying figure is the plan (actual size) of a piece of apparatus which has been devised to suspend flasks in which solutions containing heavy precipitates are being boiled. Such solutions are always in danger of bumping, and when the flasks containing them are solidly supported on the customary tripod they are frequently overturned and sometimes shattered.

The small pieces of wood ($\frac{5}{8}$" thick) have a complete circuit of string slackly threaded through oblique holes. The separate ends of another piece of string are attached to A and B, so that, after passing the arrangement over the flask, the suspension by this latter string causes the



woods to grip on to the neck, and the flask is just as firmly supported as the neck is strong.

It is obvious that so inexpensive an article may be used in numerous cases where flasks are to be temporarily suspended; all that is needed to complete the equipment being a pencil or pen-holder pushed through the longer string and laid over the hole of a filter-stand.

A rubber ring, to which string is attached, slipped over the neck of a flask, is a very handy way of suspending lighter flasks.

In any case the corrosive action of the steam or vapour from the suspended flask must be taken account of. This difficulty may be partly met for string by soaking it thoroughly in paraffin-wax, tallow, bees'-wax, or oil, rubbing it so as to leave the material in, rather than on, the string. Smooth leather, and particularly porpoise boot-laces, are very durable materials for threading and suspending the arrangement.

Pulp Filters.

Is it too much to reiterate once more the advantage of pulp filters? In some cases, mainly where large sticky precipitates are to be dealt with, the cone filter, plain or ribbed, is very necessary, but for the majority of operations the following characteristics of pulp are highly commendable:—

1. A filtering medium of any desired texture.
2. The greater effect of a given amount of wash water, since every portion thereof passes through the precipitate.
3. No fear that the precipitate will creep over the edges of the paper.

One drawback to the use of pulp is the impossibility of separating the precipitate from the paper. Happily the necessity for such a procedure is comparatively rare, and according to recent publications (Chem. News, lxxviii., 202; and *Zeit. Anal. Chemie*, 1898, xxxvii., 308) it is not necessary in some cases where it has generally been believed to be so.

Having regard to the ignition of a precipitate there is an advantage in the use of pulp in that, by thorough aspiration, the precipitate is sucked firmly on, if not into, the pulp, and is much less likely to spatter if dried rather hurriedly at the muffle's mouth.

In transferring the filter to the crucible—which is done by turning up one edge of the filter with the leg of a forcep, lifting it out, and cleaning with a piece of paper pressed against the revolving funnel—it is frequently impossible to prevent the precipitate touching the crucible at some point. In such ways the glaze of a porcelain crucible is soon destroyed.

To prevent this, it is advisable to place a piece of ash-less filter-paper in the crucible and the filter thereon; in this way only the dried precipitate can come into contact with the porcelain, and the brushing out of non-fusible compounds is generally easy and pleasant.

Accelerated Evaporation.

When a solution is being evaporated with a view to ignite the residue, the evaporative surface may be increased by placing a piece of crumpled ashless paper so that it shall be almost wholly above the surface of the liquid. This plan is, of course, not applicable to such solutions as decompose paper.

THE ELECTROLYTIC PREPARATION OF IODOFORM.

By K. ELBS and A. HERZ.

For some years the Chemische Fabrik auf Actien has been manufacturing iodoform, bromoform, and chloroform by the electrolysis of the alkaline or alkaline-earthy chlorides, bromides, and iodides in the presence of alcohol, aldehyd, or acetone. The operation is carried out warm.

For the preparation of iodoform, the electrolyte should be traversed by a current of carbonic acid during the whole of the operation. In fact, the ordinary reaction for the preparation of iodoform is as follows:—

$$CH_3CH_2OH + 10I + H_2O = CHI_3 + CO_2 + 7IH.$$

If this iodine is produced by the electrolysis of an iodide, the alkali set at liberty ought to be saturated; if not, it will again react on the iodoform. It is for this reason that carbonic acid is injected during the operation.

The authors show that the current of carbonic acid can be advantageously replaced by a simple addition of an alkaline carbonate to the electrolyte. In the present note the authors have studied the variations in the return of iodoform according to the temperature, the density of the current, &c., and they come to the following conclusions:—

1. The most favourable temperature is between 60° and 70° C. All other conditions remaining the same, the proportion of hydriodic acid formed increases as the temperature rises.

2. The return of iodoform diminishes if the density of the current exceeds 1 ampère per square decimetre.

3. All other conditions remaining the same, the return of iodoform decreases a little, and the return of hydriodic acid increases a good deal as the proportion of carbonate of soda in the electrolyte is augmented.

4. The best method consists in operating on a solution containing—

Carbonate of potassium	5 grms.
Iodide of potassium	10 ,,
Alcohol	20 c.c.
Water	100 ,,

Every hour the iodoform deposited is collected, and the strength of the solution in iodide of potassium, alcohol, and carbonate of potassium is made up to the standard.

5. The results are much less satisfactory if the alcohol is replaced by acetone. In none of their experiments have the authors obtained pure iodoform. This body was always mixed with iodine and secondary iodised derivatives.

6. Attempts to prepare bromoform and chloroform by the same process have not been successful.—*Zeit. für Electrochemie*, p. 113, 1898.

ON THE DISSOCIATION SPECTRA OF MELTED SALTS.

METALLOIDS: SILICON.

By A. DE GRAMONT.

The melted alkaline silicates give, with the usual arrangement of the apparatus already described, a very good spectrum of silicon with a medium condensation of not more than two jars (24 square decimetres). I here give the wave-lengths, corrected to Rowland's scale, I obtained either with the melted salts or with crystallised silicon in a vapour of pure hydrogen.

Si α	636·97	Strong.
	634·22	Very strong.
Si β	597·89	Fairly strong.
	596·03	Easily seen.
Si γ	506·00	Very strong.
	504·55	,,
Si δ	457·57	Very faint.
	456·89	Fairly well seen.
	455·37	Easily seen.
Si ε	413·13 / 412·92	Fairly strong, very diffuse, and almost united into one band (413·0).

The brightest and most characteristic groups are Si α in the red, Si γ in the green, and Si ε in the violet.

In examining Si γ, it is necessary to be careful not to confound it with a possible apparition of the platinum line 506·04 or with 504·57 of the air. It is for the purpose of eliminating this latter that I examined the silicon spark in hydrogen. The double line Si γ is further, more intense, and has a more diffuse appearance than the corresponding lines of air and of platinum when they appear under the same conditions of experiment.

The group Si δ corresponds to a vague band, 456·5 (Salet), and which M. Lecoq de Boisbaudran observed, as also I did, to be formed of a well-defined triplet.

The fluosilicates also furnish beautiful spectra of silicon. The natural silicates, and in general all non-conducting minerals containing silicon, when reduced to powder and melted with an alkaline carbonate—that of lithium for preference—give, with the condenser spark, not only the silicon lines, but also the spectra of the greater part of the bodies with which they are combined.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 13.

ON THE NITRIFICATION OF GLYCERIN WITH NITROUS ACIDS.

By R. AUZENAT.

Since England, by an Order in Council (No. 1, August 5, 1875), decided on the proof to which nitrated explosives intended for import into that country or her colonies should be submitted, this proof, called the heat test, has been adopted throughout the industry.

As is well known, the object of this test is to estimate the time which a certain sensitive paper takes to become discoloured, either by the acidity of the explosive or by the presence of unstable nitric ethers.

In the manufacture of nitroglycerin it is generally admitted that the product obtained with a nitrous nitric acid is so much the richer in unstable sub-derivatives of kinitroglycerin as the proportion of hyponitric acid is greater. Several specialists have also given very different opinions as to the influence exercised by the alkaline washings at a high temperature on the stability of nitroglycerin.

It is in order to throw more light on this question that I undertook the following experiments:—

Nitrifications were made with the same glycerin (of 1·262 density), the same sulphuric acid (at 97 per cent H_2SO_4), and with nitric acids containing the same proportions per cent of HNO_3 (94 per cent) but differing in their proportions of N_2O_4.

The nitroglycerin obtained was washed as usual, first several times with water, then twice with an equal volume of a solution of carbonate of soda at 4 per cent and at 60° C. The nitroglycerin was then washed with distilled water until the alkaline reaction disappeared, and filtered. It is in this state that it was submitted to the heat test; the time noted indicates the precise moment of the appearance of the typical tint on the sensitive paper.

We may as well first mention that the regulations consider as good a nitroglycerin which does not colour the paper before fifteen minutes at 71° C.

No.	N_2O_4 in the nitric acid. Per cent.	Time observed. Minutes.
1.	0·95	2, 2, 2, 2
2.	1·25	55, 55, 55, 55
3.	1·50	55, 63, 63, 72
4.	1·75	46, 46, 48, 48
5.	2·00	42, 42, 43, 47
6.	2·50	38, 38, 42, 42
7.	3·00	30, 30, 30, 34

Although the nitroglycerin No. 1 gave no acid reaction, it was again washed with a solution of 4 per cent of soda at 70° C.; the time observed was then 21, 26, 26, 27 minutes.

The nitroglycerin No. 2 re-washed with soda at 80° C. gave 63, 63, 64, 65 minutes.

No. 3 was washed at 45° C. with water containing 0·5 per cent H_2SO_4; it then had a slightly acid reaction, and answered the test at 54, 56, 56, 57 minutes.

To this same nitroglycerin No. 3, when neutral, I added 0·0006 grm. of nitric acid for each 3·24 grms. of nitroglycerin; the coloration of the paper was immediate. I then added only 0·00006 grm. of nitric acid; the coloration of the paper occurred after nineteen minutes. I increased

the quantity of nitric acid again to 0·00012 grm., and the coloration appeared at the end of fourteen minutes.

So from these results we may conclude that:—

a. Although in ordinary practice the proportion of hyponitric acid in the nitric acid is fixed at 2 per cent, we can obtain a nitroglycerin which satisfies the heat test by a nitrification carried out with a nitric acid containing 3 per cent of N_2O_4. However, above 2 per cent decompositions during the nitrification are frequent.

b. The washings with the soda solution at a high temperature increases the stability.

c. Finally, the heat test does not show any sulphuric acid acidity, which is always dangerous if the explosive is to be stored; but it enables us to reject a nitroglycerin containing more than 0·003 per cent of free nitric acid at 71° C., which is a very sensitive indication for such a body. An imperfect washing of the nitroglycerin cannot introduce a sulphuric acidity, since we have used a sulpho-nitric mixture in its manufacture, but the use of an impure absorbent may lead to the presence of a fixed free acid.

It is therefore indispensable to first treat with litmus. If the dynamite has a neutral or alkaline reaction we need not fear the presence of unstable nitric ethers, and in this case the sensitiveness of the test is sufficient.—*Moniteur Scientifique*, Series 4, vol. xii. (second part), Sept., 1898.

PRACTICAL CHEMISTRY.

By GEORGE GEORGE, A.I.C., F.C.S.

I. *A New Flask.*

In the preparation of organic compounds it is often necessary to pass into a liquid, which is kept boiling in a flask connected with a reflux condenser, a gas, which either has some direct chemical action upon the liquid or is simply used to drive out air, and thus prevent oxidation. For example, in the preparation of benzalchloride, chlorine is passed into boiling toluene.

In such an experiment the flask used has to be provided with an exceptionally large neck, in order that the inner tube of the condenser and the tube which is conducting in the gas may both pass through the cork. The flask A (Fig. 1) has been found to be much more convenient. The neck is of an ordinary size, whilst the tube B is fused into the side of the neck These flasks can be obtained from any glass-blower at a cost practically the same as that of the ordinary distilling bulb of the same size.

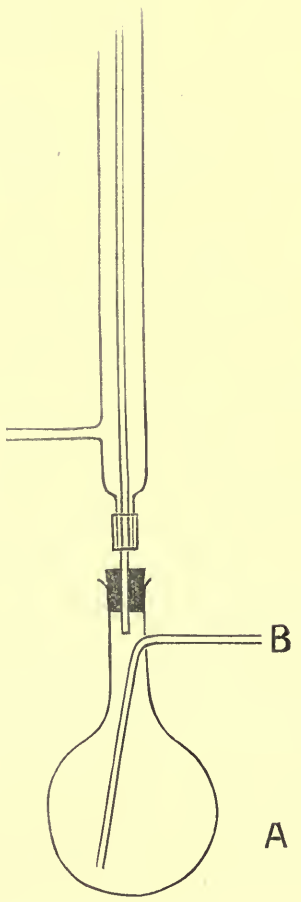


Fig. 1.

II. *Composition of Magnesium Oxide.*

In determining the composition of magnesium oxide, by heating magnesium in a porcelain crucible, unless great care is taken the results are not good, owing to the loss of oxide, and also to the formation of a quantity of nitride. A much better piece of apparatus to use than a crucible is a glass tube, as shown in Fig 2. The tube, which is about 10 c.m. long, is made from hard glass tubing of 1 c.m. diameter. The end D is drawn out, and this end is packed with dry asbestos wool (A). At C, a cork containing a small tube is fitted, whilst the magnesium is placed about the middle of the tube (B). Air or oxygen is aspirated through the tube, whilst the portion at B is heated by means of the Bunsen. The asbestos arrests any oxide that is carried over by the current of air. The experiment may be varied by using copper foil or precipitated copper.

Allan Glen's School
(Glasgow and W. of Scotland Technical College).

Note on Drown's Method of Determining Silicon in Steel.—George Auchy.—The author modifies Drown's method by conducting the evaporation with aqua regia and sulphuric acid, instead of sulphuric and nitric acids. He claims a great gain in accuracy as well as practical convenience.—*Journ. American Chem. Soc.*, vol. xx., pp. 547—549.

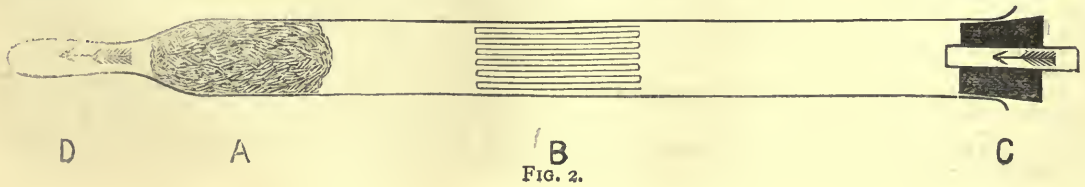


Fig. 2.

THE EXTRACTION OF NICKEL FROM ITS ORES BY THE MOND PROCESS.*

By Professor ROBERTS-AUSTEN, C.B., D.C.L., F.R S., Assoc. Inst. C.E.

THE Mond process marked an entirely new departure in metallurgical practice and in the principles which had hitherto guided it. It depended on the remarkable property possessed by nickel of forming a volatile compound with carbon monoxide, from which metallic nickel might be released if the gaseous compound was heated to 180° C.

The methods hitherto employed for extracting the metal from its ores involved concentrating the nickel either as a sulphide (matte or regulus), or as arsenide (speise), followed by either dry or wet treatment; and the metal had to be refined, mainly with a view to separate it from associated carbon.

In 1889, Dr. Ludwig Mond, in collaboration with Dr. Carl Langer, had been engaged upon a method for eliminating the carbon monoxide from gases containing hydrogen. They had been guided by the observation that finely-divided nickel removed carbon from carbon monoxide at a temperature of 350° C., converting it into carbon dioxide, whereas the dissociation of carbon monoxide by heat alone, according to Victor Meyer and Carl Langer, remained incomplete at the high temperature of 1690° C. The experiments were carried out in conjunction with Dr. Friedrich Quincke; finely-divided nickel, formed by reducing nickel oxide at 350° C. by hydrogen, being treated with pure carbon monoxide in a glass tube at varying temperatures. The gas escaping from the apparatus was ignited, and while the tube containing the nickel was cooling, the flame became luminous, and increased in luminosity as the temperature sank below 100° C. Metallic spots were deposited on a cold plate of porcelain held in this luminous flame, and on heating the tube through which the gas was escaping a metallic mirror was obtained, while the luminosity of the flame disappeared. These metallic deposits were found to be pure nickel. Nickel carbonyl was then isolated in a liquid state, and it was possible to produce it with facility in any desired quantity. It could be readily distilled without decomposition, but on being heated to 150° C., the vapour was completely dissociated, pure carbon monoxide being obtained and the nickel being deposited in a dense metallic film upon the sides of the vessel.

No other metals which were submitted to investigation showed indications of combining directly with carbon monoxide except iron. The discovery that in a mixture of metals only nickel and iron would form volatile compounds with carbon monoxide, and that they could, therefore, be separated from the other metals, induced Dr. Mond to arrange experiments with ores containing nickel, cobalt, iron, and copper—such as "kupfernickel" and "pyrrhotine." The experiments afforded such promising results that apparatus of considerable size, though still within the limits of the resources of a laboratory, was set up, and in it several pounds of ore could be treated with carbon monoxide. The principal nickel ores which were metallurgically treated contained the nickel in combination with arsenic and sulphur, besides other metals and gangue. These ores had first to be submitted to calcination, in order that the nickel might be present in the form of oxide, and to drive off, as far as practicable, the arsenic, sulphur, and other volatile bodies. The resulting oxide of nickel was treated with reducing gases, such as water-gas or producer gas, in order to convert the oxide of nickel into finely-divided metallic nickel, and the material containing it was cooled to about 50° C., and was treated with carbon monoxide.

In 1892 an experimental plant on a large scale had been erected at Smethwick, near Birmingham. The process began with "Bessemerised" matte; it ended with the market product, commercial nickel. The Bessemerised matte proceeded to the first operation of dead roasting, after which the matte contained 35 per cent of nickel, 42 per cent of copper, and about 2 per cent of iron. It then passed to the second operation for the extraction of part of the copper (about two-fifths) by sulphuric acid, the copper being sold as crystallised sulphate of copper. The residue from this process contained about 51 per cent of nickel, and it passed to the third operation for reducing the nickel. Incidentally, the remaining copper was reduced to the metallic state, care being taken to avoid reducing the iron. This was effected in a tower provided with shelves, over which mechanical rabbles passed, the reducing agent being the hydrogen contained in water-gas. The temperature did not exceed 300° C., and should be kept lower when much iron was present. From this tower the ore was conveyed continuously to the fourth operation of volatilisation, in which part of the nickel was taken off by carbon monoxide and formed the compound nickel-carbonyl. The formation of this volatile compound was effected in a tower similar to the reducing tower, but the temperature was much lower, and did not exceed 100° C. From the volatiliser, the ore was returned to the reducer, and it continued to circulate between the reducing and the volatilising stages for a period which varied between seven days and fifteen days, until about 60 per cent of the amount of nickel had been removed as nickel-carbonyl. The residue from this operation, amounting to about one-third of the original calcined matte, and not differing much from it in composition, was returned to the first operation and naturally followed the same course as before. The nickel-carbonyl produced in the fourth operation passed to a decomposer, which consisted either of a tower or a horizontal retort heated to a temperature of 180° C., so as to decompose the nickel-carbonyl and release the nickel in the metallic form, either on thin sheets of iron, or, preferably, on granules of ordinary commercial nickel. Carbon monoxide was in turn also released, and was returned to the volatiliser for taking up a fresh charge of nickel. When the operation was in progress, the gaseous carbon monoxide and the partially reduced oxide of nickel and copper continuously revolved in two separate circuits, which joined and crossed each other in the volatiliser. The commercial product contained 99·8 per cent of nickel.

The author proceeded to a description of the working as he saw it in full operation in Smethwick a few months ago. The plant had been working for some time, and about 80 tons of nickel had already been extracted from different kinds of matte. The results were quite satisfactory, and pointed to the conclusion that the process was well able to compete with any other process in use for the production of metallic nickel.

The process would always occupy a prominent position in chemical history, and there appeared to be no reason why it should not play an important part in metallurgical practice. Its application in Canada to the great nickeliferous district of Sudbury would probably contribute to the development of the resources of the great Dominion.

* Abstract of a Paper read before the Institution of Civil Engineers, November 8, 1898.

Azimidic Combinations of Benzimidazols.—St. von Niemetowski.—In a previous communication, the author showed that, by the action of nitric acid on the ortho-amidobenzimidazols, new compounds were formed, which he called azimides of the benzimidazols. He now describes many of their properties, and notes that the facility with which the avimidic chain is broken differentiates these compounds from the true azimides, which are characterised by great stability. They have further studied the azimides of (β) orthoamidophenylbenzimidazol, of (β) orthoamidophenyl, &c., as well as the action of bromine on these azimides, and the nitric colouring matters derived from them.—*Berichte der Deutschen Chemischen Gesellschaft*, xxxi., 1898.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 3rd, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Messrs. L. M. Nash, A. J. Parker, W. A. Lethbridge, F. E. Weston, and W. C. Reynolds were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Hugh Poynter Bell, 30, Egerton Crescent, S.W.; Reginald Arthur Berry, The University Chemical Laboratory, Cambridge; Thomas Henry Boardman, 4, St. George's Terrace, Wilton, Taunton; Marston Taylor Bogert, 259, Broadway, Flushing, New York; Arthur Brooke, 17, Cavendish Square, Hull; Johannes Christian Brunnich, Agricultural College, Gatton, Queensland; John Paul de Castro, Ford House, Redruth, Cornwall; David Leonard Chapman, Hulme Hall, Plymouth Grove, Manchester; William Samuel Crouch, Colombo, Ceylon; Alfred Valentine Cunnington, Christ's College, Cambridge; William Brown Davidson, 29, Bedford Street, Liverpool: Samuel Dickson, The Kraal, Elm Road, New Maldon; Francis Alfred Drake, Rivington and Blackrod Grammar School, Horwich, Lancs.; James Edward Ferguson, 26, Connaught Road, Stroud Green, N.; John Naish Goldsmith, Rock House, Tunbridge Wells; E. B. Hadley, The Green, Calne, Wilts; John Haworth, 4, Horsdon Terrace, Tiverton, Devon; Alexander Garden Hendry, 14, Avenell Road, London, N.; George William Fraser Holroyd, 14, Kensington Garden Terrace, W.; Walter Howe, 45, Spring Gardens, Bradford; Thomas Hill-Jones, Eagle Wharf Road, London; Reginald Arundale Kay, 7, The Causeway, Cambridge; John Charles Mascarenhas, 35, Harold Road, Upton Park; Thomas Arthur Nightscales, Tynemouth Street, Hull; William Pollard, Hitchin, Herts; John Armstedt Ray, jun., 15, Nassau Street, Dublin; Edmund Milton Rich, 7, Therapia Road, Honor Oak, S.E.; Gilbert Rigg, Tudor Villa, Bryn Road, Swansea; Henry John Rolfe, 8, Powis Square, Bayswater, W.; Richard Seligman, 15, Queen's Gate Gardens, S.W.; George Senior, Arwendon, Abergele, North Wales; Samuel Smiles, jun., Fairoak, Beckenham, Kent; Benjamin Jordan-Smith, 42, King's Road, Reading; Basil Steuart, Broxburn, near Edinburgh; Ambrose Walton, Gledholt, Lower Broughton Road, Broughton; John Henry Young, 115, Birmingham Road, Oldbury.

The President said that before passing to the ordinary business of the meeting, he desired, on behalf of those present, to express condolence with the family of the late Mr. J. A. R. Newlands in their bereavement. It was not the occasion to refer to the work of Mr. Newlands in detail; everyone would recognise, however, that his name would always be associated with the progress of chemical thought in our time, and, happily, he had lived to witness the expansion of the idea contained in his law of octaves into one of the most comprehensive developments of modern chemical theory. As a tribute to his memory, it was proposed that an enlarged portrait of Mr. Newlands should be hung in the Society's rooms.

Of the following papers those marked * were read:—

*117. "*Determination of the Equivalent of Cyanogen.*" By George Dean, B.A.

An examination of the different values found for the atomic weight of nitrogen led to the attempt to deduce it in another way, viz., from the equivalent of cyanogen. A known quantity of dry silver cyanide, prepared by precipitation of dilute silver sulphate solution with dilute hydrocyanic acid, was dissolved in nitric acid, and the silver determined by finding what amount of pure potassium bromide was necessary for its complete precipitation. Stas's method of titration in a beam of yellow light was employed.

The weight of cyanide corresponding to the atomic weight of silver was thus found; subtracting from this the atomic weight of silver, the equivalent weight of cyanogen was obtained. The result of the experiments performed was to give a value of 26·065. Thus cyanogen is added to those substances—*e.g.*, chlorine, bromine, iodine, &c.—whose equivalents have been observed by direct comparison with silver. If the value 12·01 is assumed to be the atomic weight of carbon, that for nitrogen, calculated from the equivalent of cyanogen, is 14·055.

Discussion.

The President referred to the great importance of determining atomic weights by indirect methods. In conjunction with Dr. Scott, he had estimated the molecular weight of triethylamine hydrobromide by titrating purified triethylamine with hydrobromic acid (*Proc. R. S.*, 1883, xxxv., 347). The values obtained showed differences which were easily recognisable, the best determination giving 182·012, and the mean 182·089 for the molecular weight. This proved that triethylamine could not as yet be obtained sufficiently pure for the purpose of a determination comparable in accuracy with Stas's determination of the ammonium salt; but in spite of the relatively wide limits, it was possible to deduce the atomic weight of carbon from these values by a method entirely independent of the combustion of carbon as diamond, graphite, or carbonic oxide, on which all previous determinations of the atomic weight of carbon had been based. Thus subtracting Stas's value for the molecular weight of ammonium bromide (98·032), the values for C_6H_{12} became 83·98 and 84·057 respectively, which lead to 11·981 and 11·993 as the atomic weight of carbon if Stas's value for hydrogen (1·008) be employed. Stas, curiously enough, had never deduced the atomic weight of hydrogen from his values for ammonium and nitrogen. The probable explanation of this was that he believed the deduced result, O : H = 16 : 1·008, to be far too high, being unable to reconcile it with the determination O : H = 16 : 1, which Dumas obtained from the synthesis of water. If, however, the atomic weight of hydrogen be taken as unity, Stas's values for oxygen and nitrogen become 15·86 and 13·92 respectively, and it was to be remembered that, according to Lord Rayleigh, the densities of hydrogen and nitrogen were in the ratio of 1 to 13·898. Mr. Dean's experiments gave for the atomic weight of nitrogen a value slightly higher than this, and almost identical with that deduced by Stas for his synthesis of fused nitrate of silver. He hoped Mr. Dean would continue this important research.

*118. "*The Composition of American Petroleum.*" By Sydney Young, D.Sc., F.R.S.

An investigation has been made of the hydrocarbons in American petroleum boiling between, say, 25° and 115°, and evidence has been obtained of the presence of the following:—

Isopentane, b. p. 27·95°; normal pentane, b. p. 36·3°; pentamethylene, b. p. about 50°; isohexane, b. p. about 61°; normal hexane, b. p. 68·95°; methylpentamethylene, b. p. about 72°; benzene, b. p. 80·2°; hexamethylene, b. p. 80·8°; isoheptane, b. p. 90·3°; normal heptane, b. p. 98·4°; methylhexamethylene, b. p. about 102°; toluene, b. p. 110·8°. Of these, the two pentanes and normal hexane have been obtained pure, normal heptane nearly so, and hexamethylene and isoheptane fairly pure. Miss E. C. Fortey, B.Sc., has obtained hexamethylene nearly pure from American and quite pure from Galician petroleum (*Proc.*, 1898, xiv., 103). It is not improbable that other isomeric hexanes, and, therefore, possibly heptanes, may be present, and there are indications of the existence of small quantities of dimethylpentamethylene in American petroleum. A comparison of the results obtained with American, Galician, and Russian petroleum shows that the same classes of hydrocarbons—paraffins, polymethylenes or naphthenes, and aromatic hydrocarbons—are present in the petroleum from all three sources, but

that the relative amount of naphthenes, and, in all probability, of aromatic hydrocarbons, is greatest in Russian and least in American petroleums.

*119. "*The Separation of Normal and Iso-heptane from American Petroleum.*" By FRANCIS E. FRANCIS, B.Sc., Ph.D., and SYDNEY YOUNG, D.Sc., F.R.S.

The heptanes cannot be separated in a pure state from petroleum by fractional distillation, owing to the presence of naphthenes with boiling-points not sufficiently far removed from those of the two paraffins.

A large quantity of mixed heptanes containing naphthenes, obtained by the partial fractionation of American petroleum, was therefore brominated. Heptyl and isoheptyl bromides were separated by fractional distillation under reduced pressure with a twelve-column dephlegmator, and were reduced in alcoholic solution by a copper-zinc couple, a small amount of saturated hydrochloric acid being added. The reduced hydrocarbons were purified as far as possible, but the quantities — especially that of isoheptane—were too small to admit of satisfactory fractionation.

The boiling-points and specific gravities of both paraffins were determined, also the critical constants of normal heptane, and its vapour pressures and specific volumes at a few temperatures. The data are compared with those for Thorpe's specimens of normal and isoheptane.

*120. "*The Boiling-points and Specific Gravities of Mixtures of Benzene and Normal Hexane.*" By D. HAMILTON JACKSON, M.A., Ph.D., and SYDNEY YOUNG, D.Sc., F.R.S.

In the fractionation of American petroleum from which the aromatic hydrocarbons have not been removed previously by treatment with a mixture of sulphuric and nitric acids, it is noticed that the benzene comes over chiefly at about 65°, the fractions above and below this temperature containing smaller and smaller amounts of it.

The approximate estimate of the amount of benzene is easily obtained by treating the fractions repeatedly with mixed nitric and sulphuric acids and diluting the acid with water. The dinitrobenzene separates after some time in needle-shaped crystals. The most probable explanation of the lowering of the boiling-point of benzene appeared to be that aromatic hydrocarbons and paraffins, though miscible in all proportions, approximate in their behaviour to partially miscible liquids. The results obtained show that this is the case, for there is always expansion on mixing, and the boiling-point of normal hexane is hardly raised by the addition of even 10 per cent of benzene, whilst that of benzene is very rapidly lowered by adding hexane.

It is therefore impossible to separate pure normal hexane by distillation of any mixture of this paraffin with benzene, though it is easy to separate pure benzene from a mixture containing only a moderate amount of hexane.

*121. "*The Action of Fuming Nitric Acid on the Paraffins and other Hydrocarbons.*" By FRANCIS E. FRANCIS, B.Sc., Ph.D., and SYDNEY YOUNG, D.Sc., F.R.S.

In the separation of pure normal hexane from American petroleum, the methyl pentamethylene was removed by heating the nearly pure hydrocarbon with fuming nitric acid during several days. It was observed at the same time that the low boiling fractions, containing isohexane, were also purified by this treatment, and that, on diluting the nitric acid, considerable quantities of a trinitro-derivative of isohexane separated as a crystalline solid.

Other isoparaffins were found to react rapidly with fuming nitric acid when heated on a water-bath, and to yield liquid or solid nitro-compounds, but the normal paraffins were attacked only very slowly, and in these cases the acid, when diluted, did not become turbid. Details are given of the action of fuming nitric acid on isopentane, isohexane, isoheptane, iso-octane, and diisobutyl.

The behaviour of the paraffins, when heated with fuming nitric acid, is compared with that of other classes of hydrocarbons.

DISCUSSION.

Mr. GROVES asked to what extent olefines were present in petroleum.

Mr. DAVIS referred to Worstall's statement that normal hexane yields a considerable amount of the primary nitro-derivative when boiled with fuming nitric acid during a long period (*Amer. Chem. J.*, 1898, xx., 202), and asked whether this had been observed by the authors, as such a method of purifying normal hexane would appear to be rather destructive.

Professor YOUNG, in reply, said that the olefines present in American petroleum must be inconsiderable in amount, as very little bromine is required to produce a permanent colouration; they would, of course, be eliminated during the treatment with mixed nitric and sulphuric acids.

With respect to the action of nitric acid, it must be remembered that the result is greatly influenced by the conditions; thus Konowaloff had shown that normal hexane and normal octane yield secondary nitro-compounds on heating with dilute nitric acid under pressure. Dr. Francis and he had found that the isoparaffins undergo nitration readily when heated with fuming nitric acid in a reflux apparatus on a water-bath. The normal paraffins were much more slowly attacked under similar conditions, and as the nitric acid remained clear on dilution, it was evident that nitro-compounds had not been formed from them in any appreciable quantity.

*122. "*A Composite Sodium Chlorate Crystal in which the Twin Law is not followed.*" By WILLIAM JACKSON POPE.

The author describes a composite crystal of sodium chlorate deposited from a pure aqueous solution. It consists of a cube-shaped crystal growing on to a tabular one; both crystals show the form $\{100\}$; a three-fold axis of symmetry of the one coincides in direction with a four-fold axis of symmetry of the other, and the plane (011) on the former is parallel to the plane (010) on the latter. The composite crystal is thus not developed in accordance with the ordinary twin law, and yet the two crystalline individuals have grown together in a highly symmetrical manner.

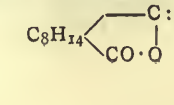
*123. "*Stereoisomeric Bromonitro- and Chloronitro-camphors.*" By T. MARTIN LOWRY, B.Sc.

The action of nitric acid on bromocamphor and on chlorocamphor leads to the production of only one nitro-bromo- and nitrochloro-camphor. The action of bromine and of chlorine on an alkaline solution of nitrocamphor yields in each case, however, a mixture of stereoisomerides, similar to that which is produced by the action of bromine on chlorocamphor (*Trans.*, 1898, lxxiii., 569). The stereoisomeric bromonitro- and chloronitro-camphors, isolated from this mixture, have the following melting-points and specific rotatory powers:—

	M.p.	$[\alpha]_D$(chloroform).
α-Chloro-α'-nitrocamphor	95°	− 5°
α'-Chloro-α-nitrocamphor	132	+13
α-Bromo α'-nitrocamphor	107	−22
α'-Bromo-α-nitrocamphor	106	+53

*124. "*Camphoryloxime* (*Camphonitrophenol*)." By T. MARTIN LOWRY, B.Sc.

The so-called "camphonitrophenol," produced by boiling nitrocamphor with concentrated hydrochloric acid, is shown to be an oxime of camphoric anhydride, identical with that obtained by the interaction of hydroxylamine with camphoric anhydride. Its constitution is probably that represented by the formula—



125. "*The Formation of Ethereal Salts of Polycarboxylic Acids.* By S. Ruhemann and A. V. Cunnington.

The authors have found that the condensation of ethylic malonate and its homologues with the ethylic salts of unsaturated acids, leading to the formation of those of polycarboxylic acids, is readily brought about by adding a small quantity of sodium ethoxide (0·5 grm.) to the mixture of ethereal salts. In a number of cases the combination is accompanied by an evolution of heat, the intensity of which appears to depend on the negative character of the salts entering into reaction.

The preparation of a number of salts of polycarboxylic acids by this method is described, and the conclusion is drawn that in the same measure as the negative character is diminished by the introduction of an alkyl radicle into ethylic malonate or the ethylic salt of the unsaturated acid, so does the heat evolved in the reaction decrease.

126. "*Note on the Action of Light on Platinum, Gold, and Silver Chlorides.*" By E. Sonstadt.

The action of direct sunlight on very dilute solutions of potassium chloroplatinate is similar to that of prolonged heating, platinum monochloride being separated, as described in an earlier paper (*Proc.*, 1898, xiv., 25). The action of bright sunshine is, however, slower and feebler than that of heat. Solutions of gold chloride, if sufficiently dilute, are more readily affected by light than corresponding platinum solutions. An aqueous solution containing about 0·04 per cent of gold chloride required exposure to bright sunshine for a day or two before any action was perceptible, and the reduction was incomplete even after exposure during several weeks. A more dilute solution, containing 0·007 per cent of gold chloride, became distinctly bluish after a few hours' exposure, and the blue colouration deepened day by day until a deposit formed, which was blue by transmitted light, and afterwards assumed the usual brown colour of precipitated gold, the liquid being left colourless. A trace of hydrogen peroxide was detected in the liquid. The reaction may therefore be considered to be the same in this case as when a very dilute solution of auric chloride is decomposed by heat (Chem. News, 1898, lxxvii., 74).

It seemed probable that the action of light on silver chloride would, like the decomposition of platinum and gold chlorides in dilute solution by the action of heat or of light, depend on the presence of water and the formation of hydrochloric acid and hydrogen peroxide. Some silver chloride, precipitated from solution of silver nitrate by hydrochloric acid, was thoroughly washed by agitation with repeated portions of water, and decantation, the operations being conducted by feeble gas light, and then exposed under water to direct sunlight, with frequent agitation. After some days the supernatant water was examined, and was found to contain a very appreciable quantity of hydrochloric acid, and to give a faint reaction for hydrogen peroxide. One of the two formulæ which will satisfy these conditions is—

$$6AgCl+4H_2O=2Ag_2Cl+2Ag+2H_2O_2+4HCl.$$

But as silver, set free molecularly in presence of hydrochloric acid, would, on a reasonable presumption, form silver chloride with liberation of hydrogen, and as the nascent hydrogen would react on part of the hydrogen peroxide to form water, the equation, with these corrections, becomes—

$$6AgCl+4H_2O=2Ag_2Cl+2AgCl+2HCl+2H_2O+H_2O_2.$$

The same series of reactions would occur with the reformed silver chloride and water; and it is obvious that, as, at each stage of the reaction, one-third of the silver chloride and one-half of the water are reproduced, and similarly with the hydrochloric acid and hydrogen peroxide, it follows that when the silver chloride taking part in the reaction is completely converted into argentous chloride, water will still be left as a permanent residue in addition to hydrochloric acid and hydrogen peroxide. This assumes that the silver chloride in a condition of accessibility to the influence of light is in the exact proportion to the water present indicated in the equation. But if the attackable silver chloride is present in a certain excess over that required by the equation, the end products of the series of reactions may be represented by the simple equation—

$$4AgCl+2H_2O=2Ag_2Cl+2HCl+H_2O_2,$$

in which no residue of water appears. This is the second of the two possible formulæ referred to, and, it may be asked, what need is there to assume the complex reactions in series following from the first formula, when the second, which is so much simpler, satisfies the experimental results? There are, however, other experimental results of a singular character to be described, which may possibly be considered to be more easily intelligible on the supposition that the reactions are of the serial nature involved in the first equation.

Some silver chloride, precipitated and washed as already described, was dried for several hours on a sand-bath, the temperature being raised progressively until the chloride became adhesive. Although the process was conducted under very feeble gas light, the chloride was sensibly discoloured. This discolouration is probably due to the same reaction taking place between moisture and the chloride under the influence of a high temperature as is effected by light in the cold. It appears that a higher temperature is needed for the reaction than that of water boiling at ordinary pressure, as the chloride is not discoloured by heating under water. A thoroughly dry and heated glass tube was nearly filled with the hot chloride, and immediately sealed. Another portion of the chloride was put into a bulb tube which had been previously dried and strongly heated, and was fused in the bulb. A slight, but unmistakable, trace of moisture condensed on the sides of the tube, showing that the chloride was not perfectly dry. The tube containing the (imperfectly) dried silver chloride was exposed to direct sunshine, when a bluish tint instantly spread over the chloride, deepening to a rusty brown, but leaving patches unaffected, so that, after long exposure, the fragments presented a mottled appearance with white spots on a dark ground. Evidently, portions of the chloride were really dry, though the bulk was not so, the dry portions resisting the action of light. Another tube, rather long and narrow, was similarly filled with the dried chloride, sealed, and exposed to sunshine with about half its length covered. The exposed portion of the chloride darkened as in the former case, with patches remaining unaffected. The covering was then shifted over the previously exposed part of the tube, with a like result; but the darkened chloride, now sheltered from light, became slowly bleached, until it was quite white. On again reversing the conditions, the bleached portion darkened and the coloured portion was bleached, the same happening on each subsequent reversal. Even in the portion of the tube exposed to bright sunshine, the chloride on the under side became partially bleached, and on turning the tube round, the effect, after a few hours, was reversed. Dry silver chloride was then placed in the central part of a phial tube, and was protected by a little recently ignited asbestos from contact with fragments (placed in its lower and upper parts) of calcium chloride, and of caustic soda taken from sodium that had been long kept in a loosely closed bottle. The well-closed phial was kept in the dark during two or three days, to give time for absorption of moisture, and was then exposed to sunshine. The silver chloride became coloured, with white spots remaining unattacked, as in the former cases: but, on transference to a dark place, or on shading a portion, there was no bleaching. The colouration remained practically constant in light and in shade. The bleaching effect, or the re-formation of argentic from argentous chloride under the conditions described in the former case, must therefore be attributed to a reversal in the dark of the primary reaction which takes place in the light,—a reversal made impossible in the last-mentioned case by the absorptive

action of the calcium chloride and the soda. Hydrochloric acid has no bleaching effect on light-altered silver chloride suspended in water, either in darkness or in light.

127. "*Methane Trisulphonic Acid.*" By ERNEST H. BAGNALL, B.Sc.

In endeavouring to prepare the various sulphonic acids and sulphones of dichlorobenzidine by the action of fuming sulphuric acid on dichlorodiacetylbenzidine, a substance was obtained which proved to be identical with methanetrisulphonic acid (Theilkuhl, *Annalen*, 1868, cxlvii., 134). This acid is also formed by a like process from diacetylbenzidine, acet-α-naphthalide, and acetanilide, the last giving a remarkably good yield of the substance. The silver salt crystallised in small, white, iridescent, monhydrated, orthorhombic plates, $a : b : c = 2{\cdot}9152 : 1 : 0{\cdot}5422$. The copper, barium, calcium, potassium, sodium, and ammonium salts are also described.

Attempts were made to prepare the corresponding sulphonic acids of ethane and propane by a similar process, but without satisfactory results.

128. "*The Nutrition of Yeast.*" By ARTHUR L. STERN, D.Sc.

This investigation was undertaken to determine the amount of inorganic and nitrogenous nutriment required to produce the largest crop of yeast, the greatest assimilation of nitrogen, and the most complete fermentation in a fixed time. During the course of the investigation other points had to be considered, of which the most important was the part played by sulphur compounds on yeast nutrition. The earlier work of Hayduck, who employed a different variety of yeast and a different variety of sugar, is referred (*Zeitschrift fur Spiritusind.*, 1881, 173).

The yeast employed was a pure form obtained from a Burton pitching yeast, the sugar was *d*-glucose, the nitrogenous nutriment asparagine, and the inorganic nutriment of two kinds,—the first prepared from a yeast ash and free from sulphur, the second a mixture of potassium phosphate, magnesium sulphate, and calcium sulphate. Each experiment consisted in fermenting 500 c.c. of a 10 per cent solution of the sugar, to which varying amounts of the nitrogenous and inorganic nutriment had been added.

It is shown that sulphur is an essential constituent of yeast nutriment, and that in the absence of other more suitable forms of sulphur nutriment, sulphates can supply the yeast with this element, a portion of the sulphate being invariably reduced to sulphuretted hydrogen. Attempts were made to find a substance of known constitution which could supply yeast with sulphur without the evolution of sulphuretted hydrogen, but without success.

It has been asserted that iron is an essential constituent of yeast nutriment, but no evidence could be obtained in support of this statement.

The author has examined the effect of variation in the amount of (1) nitrogen nutriment and (2) inorganic nutriment respectively on the amount of nitrogen assimilated, the percentage of nitrogen nutriment assimilated, the percentage of nitrogen contained in the yeast, the percentage of sugar remaining unfermented, and the weight of the yeast crop, and draws the following conclusions;—Any increase of nutriment beyond a definite limit will not materially increase the amount of nitrogen assimilated by the yeast, the percentage of nitrogen in the yeast, the weight of the yeast, or the amount of sugar fermented. This limit, called the normal supply, is the largest quantity that the yeast can assimilate under the conditions employed in the experiments, and is approximately 0·025 grm. of inorganic nutriment per 100 c.c., and the same weight of nitrogen supplied as asparagine.

(To be continued).

NOTICES OF BOOKS.

Lighting by Acetylene. Generators, Burners, and Electric Furnaces. By WILLIAM C. GIBBS, M.E. London: Crosby Lockwood and Son. New York: D. Van Nostrand Company. 1898. Pp. 141.

THE production of carbide of calcium on the large scale, and by its means the subsequent production of acetylene gas, is a comparatively recent industry—and, in fact, lighting by acetylene is as yet only in its infancy. The question of generators to safely keep up a constant supply of acetylene without any intermission has not yet been solved in a perfectly satisfactory manner; but many experimenters are at work, and new schemes, as well as improvements on old ones, are constantly being brought out.

Acetylene was discovered by Edmond Davy in the year 1836; but it is only within the last few years that the commercial production of calcium carbide has brought acetylene within the range of practical utility.

The dangers attending the use of acetylene have no doubt been unduly exaggerated; heat, flame, the electric spark, or even the electric arc itself, will not produce an explosion at the ordinary atmospheric pressure; nothing but the detonation of fulminate of mercury or other violent explosive will bring this about. But when the gas is compressed, it becomes more and more unstable as the pressure increases, until the point of liquefaction is reached, when it becomes exceedingly dangerous. The use of copper must be absolutely prohibited in any apparatus or fittings with which the gas may come in contact—acetylide of copper being very explosive.

Many methods for preparing and utilising acetylene gas are fully described in this volume, the text being interspersed with numerous illustrations.

A considerable amount of space is devoted to generators, which are divided into three classes:—1st. Those which have a separate gas holder, and in which the water is supplied gradually and in measured quantity to a considerable portion of carbide; 2nd, those which contain both the carbide and the water, with means for successively immersing and withdrawing the carbide; and 3rd, those in which measured quantities of the carbide can be dropped into a large quantity of water.

Towards the end of the book, the requirements of the New York Board of Fire Underwriters are given in full, both with regard to the installation and use of acetylene gas generators, and for the storage of a limited supply of calcium carbide. There is also an imposing list of patents taken out in the United States in connection with the subject; it fills six pages in small type.

There is, we are sorry to see, no index, and the chapters are not numbered. The book is, however, well got up, and contains a great deal of valuable information.

Health Notes, and Curiosities of Medical Science. By Dr. T. L. PHIPSON. London: George Routledge and Sons, Lim. 1898. Pp. 205.

THE volume now before us gives, in an interesting and popular manner, a large amount of information with regard to health and the way to keep healthy, &c.

The book is divided into thirty-five chapters, and includes a great variety of subjects, such as the value of trees in towns from the hygienic point of view; the tobacco question with regard to disinfection—in this chapter we read that smoking is forbidden in German bacteriological laboratories, as tobacco acts injuriously on bacterial cultivations. The intelligence of beasts is an interesting chapter, as is also the one on skin grafting.

Chapter X. gives a full account of the invention and development of the thermometer, which was used in medicine two hundred and forty years ago.

The subject of "hypnotism" and "suggestion" is dis-

cussed in Chapter XIV. Cases are mentioned of surgical operations having been successfully performed without the use of chloroform, the patient being first put into a mesmeric sleep. A most remarkable case of "suggestion" is cited, where a youth is told to warm his arm at a *cold* stove; he, thinking that the stove is hot, puts his arm too near it, and actually burns himself badly, a severe blister being formed surrounded by a zone of inflammation, *just as if it had been placed in close proximity to a hot stove.* We think this tale must be taken with a certain amount of salt.

Insanity and sunstroke are treated in Chapters XVII. and XVIII., and in Chapter XXII. we come to the great water question. We are glad to see that the author has no reason to complain of the water supplied by the London water companies; it is probably the best supply in the world, and certainly no other supply is so carefully and constantly controlled and kept up to the highest standard of purity by daily chemical and bacteriological examinations.

A curious and valuable statement is to be found in Chapter XXXI. to the effect that in Normandy, where cider is practically the sole and universal beverage, the medical practitioners have *never met with a single case of stone, gravel, or calculus* during an experience of over forty years.

The book is well printed on good paper, and will well repay reading.

CORRESPONDENCE.

THE GASES OF THE ATMOSPHERE.

To the Editor of the Chemical News.

Sir,—In a Lecture delivered on the 8th of this month, at the meeting of the Pharmaceutical Society, Professor Ramsay is reported to have made the following statement:—

"Early in 1894 Lord Rayleigh wrote to *Nature*, announcing what appeared to him to be an anomaly, namely, that whilst atmospheric nitrogen was a little over fourteen times as heavy as hydrogen, nitrogen prepared from ammonia or from other chemical compounds was slightly lighter, the difference being about 1 in 230. No explanation was forthcoming at the time, but Lord Rayleigh talked the matter over with several of his friends, including the lecturer, who had some time before suggested to him, at his request, a method of preparing nitrogen by passing a mixture of air and ammonia over red-hot copper, when the oxygen united with the hydrogen of the ammonia, and the nitrogen from both the air and the ammonia passed on. He suggested to Lord Rayleigh that probably atmospheric nitrogen was not as pure as it was supposed to be, and directed his attention to Cavendish's experiments and the residue he had found when combining nitrogen with oxygen. Lord Rayleigh did not at first attach much weight to the suggestion, and thought it more likely that different compounds contained different kinds of nitrogen."

I have on previous occasions noted in your columns the progressive eclipse of Lord Rayleigh by the other member of the binary star of Argon, but I confess I was rather surprised to find him thus finally reduced to the position of the dark attendant.

On turning to Lord Rayleigh's account of the same period, given on April 5, 1895, at the Royal Institution, some rather remarkable discrepancies are revealed. Lord Rayleigh stated that, "about this time last year or a little earlier," he had been led, by his own purely physical experiments, to ask himself what was the evidence that all the so-called nitrogen of the air was of one quality? He put that question not to Professor Ramsay, but to his colleague Professor Dewar. "His answer was that he doubted whether anything material had been done upon the matter since the time of Cavendish, and that I had better refer to Cavendish's original paper." Lord Rayleigh added that he quickly followed Professor Dewar's advice, and found to his surprise that Cavendish had put the question quite as sharply as he could put it himself, and had moreover endeavoured to answer it by an appeal to experiment. He then went on to make it absolutely clear that Professor Ramsay did not appear upon the scene at all until after Lord Rayleigh, acting upon Professor Dewar's information, had found in the experiment of Cavendish the solution of his problem, and had recognised in the Cavendish residue the unknown substance hitherto confounded with nitrogen, whose presence explains the greater density of "nitrogen" obtained from the atmosphere. Hence the evidence of Lord Rayleigh given more than three years ago directly controverts the story Professor Ramsay now tells.

Again, Professor Ramsay says that "early in 1894 Lord Rayleigh wrote to *Nature*" stating the discrepancy he had found between the weights of atmospheric and chemical nitrogen, and asking chemists for suggestions. I thought it well to verify this reference. Lord Rayleigh wrote no such letter to *Nature* early in 1894. It was on Sept. 29, 1892, that the letter in question appeared. The correction is important because in his lecture, and still more distinctly in his book on the gases of the atmosphere, Professor Ramsay conveys the impression that this letter immediately led to his "asking and obtaining permission" to study atmospheric nitrogen. He tells us in the book that he began this study by passing nitrogen from the air over red-hot magnesium, and that the first weighing of a portion of gas so treated took place in May, 1894. It is obvious that this story loses considerably in plausibility when we know that the letter appeared eighteen months previously.

Did Professor Ramsay before May, 1894, ask and obtain Lord Rayleigh's consent to his concurrent investigation of atmospheric nitrogen? There is no evidence whatever for the statement. The real sequence of events I suggest is as follows:—The letter in *Nature* in 1892 had nothing to do with the matter except as an *ex post facto* excuse. In April, 1894, Lord Rayleigh read at the Royal Society a paper "On an Anomaly encountered in Determination of the Density of Nitrogen Gas." At the same time tne Smithsonian Institution was offering a prize for the most important discovery in connection with the atmosphere. Professor Ramsay took Lord Rayleigh's proof that there is some inert gas in the air which is not nitrogen, and proceeded in his own way, and without saying a word about it, to isolate and study this body. At the same time—that is, between April and July, 1894—Lord Rayleigh was pursuing the line of the Cavendish experiment, isolated the unknown gas, examined its spectrum, and showed it privately to some of his friends. It was when he was thus maturing a discovery practically made some time before, that Professor Ramsay, probably about the middle of July, came down upon him with another set of researches, springing, like his own, from the results published by himself on April 19. It can easily be understood that, as stated in Professor Ramsay's book, letters passed between them almost daily. The net result was that at the meeting of the British Association, in August, the discovery was announced in their joint names. It will be conceded, I think, that Lord Rayleigh paid heavily for the suggestion made to him two years earlier by Professor Ramsay, that he could obtain nitrogen by passing a mixture of air and ammonia over red-hot copper. From the way it is put in the lecture one might fancy that Professor Ramsay invented that bit of text-book knowledge for the occasion.

In his book on the gases of the atmosphere, Professor Ramsay, by dint of a narrative chronologically confused and a judicious abstention from precise dates, managed to convey a general impression that he had done important

and even decisive work before Lord Rayleigh had got as far as the Cavendish experiment. But he has now gone a step further, and has tried to make it appear that everything was due to his direct inspiration. If the myth goes on evolving itself at the present rate, Lord Rayleigh will shortly figure as a sort of humble assistant called in by Professor Ramsay to perform the routine work of burning away the nitrogen.

Lord Rayleigh has apparently elected to say as little as possible about the manner in which Professor Ramsay became his collaborator, but he has never admitted the accuracy of Professor Ramsay's version. One thing, however, he is quite explicit about—that the inert ingredient of the atmosphere, isolated by Cavendish, was re-discovered by himself, and recognised as something not nitrogen, before Professor Ramsay had anything to do with the matter.—I am, &c.,

SUUM CUIQUE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvi., No. 3, July 18, 1898.

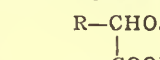
Researches on the Relations existing between Luminous Energy and Chemical Energy.—M. Berthelot.—A measure of the light energy transformed into chemical energy is best obtained by investigation of endothermic reactions, including the phenomena of oxidation or of combination, where heat is evolved. The author examines the following endothermic reactions:—Decomposition of (1) nitric acid; (2) pure iodic acid; (3) hydriodic acid; (4) oxide of mercury. Also he makes experiments on the reduction of silver chloride. All these observations take place at ordinary temperatures in—(1) direct solar light; (2) diffused light; (3) darkness. The numbers are given in the various cases.

Anhydrous and Crystallised Sulphide of Magnesium.—A. Mourlot.—The author prepares amorphous sulphide of magnesium by the action of carbon disulphide on magnesium at a red heat. The crystalline form is obtained from this by fusing it in the electric furnace, or it can also be made by the action of tin sulphide on anhydrous magnesium chlorine. In properties it differs from the amorphous form in being much more stable. It resembles crystalline barium sulphide in most of its reactions. It can, however, be easily distinguished, as it cannot be reduced by carbon.

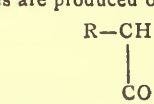
Decomposition of Barium and Calcium Phosphate by Water at 100°.—Georges Viard.—Varying weights of the phosphate are placed in the same volume of water and kept for five hours in a vessel of boiling water. The liquid is then filtered from the crystalline precipitate which is formed. Both filtrate and precipitate are analysed. It is found that the decomposition becomes more and more slow as the concentration increases. In fact the substance behaves in precisely the same way as when placed in cold water, which action was investigated by Joly; the difference being in the numbers for the ratio of the total phosphoric acid to the combined acid, the limits being 2 at 15° and 2·8 at 100°.

The Substituent Action of the Halogens upon each other in the Aromatic Series.—V. Thomas.—In a recent publication the author has shown that the whole series of substitution products of benzene, up to the compound C_6Cl_6, can be obtained by chlorination of benzene with ferric chloride, and that similar derivatives of benzene homologues, such as toluene, and of bodies with more complex molecules, *e.g.*, naphthalene, are also obtainable. Brominated benzenes also give rise to a series of chlorinated substitution products when acted upon by ferric chloride, *e.g.*, the compound C_6H_4ClBr. parabromochlorobenzene, the chlorination of which is here discussed. The ferric chloride exchanges its chlorine for the bromine of the organic bromide; an unusual phenomenon in the aromatic series, but one which is well known in the fatty series, when the chlorinating agents are metallic chlorides, such as $SbCl_5$, PCl_5, $HgCl_2$, &c. The reaction under discussion is between paradibromobenzene and ferric chloride; more than one product is obtained, each being derived from chlorination of $C_6H_4ClBr(1.4)$, but that produced in the greatest quantity corresponds to the formula C_6BrCl_5. Thus there are two stages in the reaction, viz., substitution of one bromine atom and chlorination. It is not yet determined in which order these operations occur.

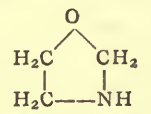
Diketones of the Tetra-hydro-β-oxazol Derivatives of the Phenylurethanes of certain Oxy-acids.—E. Lambling.—The author has demonstrated the production of urethanes of the general formula—



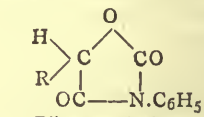
by the action of phenyl isocyanate upon esters of hydroxy-acids. The free acids are obtained by saponification with soda and subsequent decomposition of the sodium salt with acid. On boiling these acids with water, internal anhydrides are produced of the type—



which represent diketones of tetra-hydro-β-oxazol—



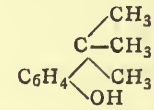
Tetra-hydro-β-oxazol.



Diketones obtained.

The author has obtained such diketones from phenylurethanes of lactic, trichlorlactic, glycolic, phenylglycolic, and α-oxyisobutyric acids. Descriptions of the properties of these substances are given.

Action of Bromine in presence of Aluminium Bromide on Para-isobutyl-phenol. Remarks on the Bromination of Phenols.—F. Bodroux.—The author has already studied the action of an excess of bromine in presence of aluminium bromide on certain phenols. He now concludes by applying the reaction to a compound possessing a long side chain, viz., para-isobutyl-phenol—



A description of the method is given and of the properties of the resulting compound. The melting-point together with the result of an estimation of the bromine it contains show that the principal product is pentabromophenol. Hence the molecule of the isobutylphenol has been split up by the action of excess of bromine in presence of aluminium bromide. The conclusion drawn is that the same rules apply, on bromination, to both hydrocarbons and phenols as regards (1) substitution of the hydrogen atoms of the benzene nucleus, and (2) replacement of the side chain—if the latter is attached by $(C)^{IV}$ or $(CH)'''$—by a bromine atom. If, on the contrary, the side chain is attached by

a (CH_2)" group it is not destroyed. Thus, in the case of certain phenols, bromination may serve to determine the constitution of the side chain.

Vol. cxxvii., No. 4, July 25, 1898.

Determination of Arsenic in Antimony and other Metals.—O. Ducru.—Already inserted in full.

Composition of Phosphorescent Sulphides of Strontium.—José Rodriguez Mourelo.—In a former paper, the author stated that monosulphide of strontium is a non-phosphorescent substance. The object of his present research is to determine what impurities cause it to appear phosphorescent. The sulphide is prepared in two ways:—1. By the reduction of celestine containing calcium sulphate and sodium chloride, in addition to strontium sulphate, by pure carbon. The resulting sulphide phosphoresces with a dull green colour. 2. By similarly treating an artificial strontium sulphate, made by precipitating nitrate of strontium with a solution of sodium sulphate. This sulphide, when pure, gives no phosphorescence, but the phosphorescence begins when sodium sulphide, sodium chloride, and strontium sulphate are added; the proportion of the latter being increased until phosphorescence ceases.

Estimation of Methyl Alcohol in Ethyl Alcohol.—A. Gautier.—The author describes a colorimetric method of detecting and estimating methyl alcohol in ethyl alcohol by means of oxidation. The reactions of the pure alcohols were first studied separately, when oxidised with potassium bichromate and sulphuric acid. Besides acetic aldehyd and acetic acid, the distillation products contained, in the one case ethylal, $CH_3.CH<^{C_2H_5O}_{C_2H_5O}$, and in the other, methylal, $CH_2<^{CH_3O}_{CH_3O}$. In order to distinguish between these two ethers, they were condensed with dimethylaniline. The resulting compounds were—(1) $C<^{H}_{CH_3}=\left(C_6H_4N<^{CH_3}_{CH_3}\right)_2$, which on oxidation gave a blue coloration, rapidly disappearing under the influence of heat; and (2) $CH_2=\left(C_6H_4N<^{CH_3}_{CH_3}\right)_2$, viz., tetramethyldiamidodiphenylmethane, which on oxidation gave an intense blue coloration, deepening under the influence of heat. By this method, a quantity of methyl alcohol not exceeding 0·5 per cent can be detected in absolute alcohol. A source of error is due to the presence of methyl alcohol existing as an impurity in the dimethylaniline, and an account is given of the means by which this is avoided.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., February 28, 1898.

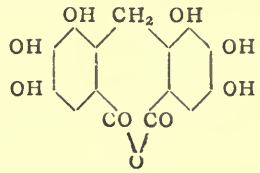
On Fluorescent Bodies.—Br. Pawlewski.—It has been laid down that, besides the anthracene derivatives and those containing sulphur and nitrogen, all fluorescent bodies should also contain a pyronic nucleus surrounded by complex atoms, and a phthalic residue. The author shows that though this theory applies to the combinations of the group of fluorescein, it is not quite the same for many other bodies. He gives as examples resorcinbenzene, allofluorescein, and benzylgaïacol. He has recently prepared a substance which possesses a very strong fluorescence; 1 part in 31,250,000 through a thickness of 15 c.c. showing a distinct fluorescence.

Products of Condensation of Furfurol and Furfuracrolein.—H. Röhmer.—The author has prepared several products of condensation, among which may be mentioned *furalpyruvic acid*, $C_4H_3O.CH=CH.CO.COOH$, obtained by the condensation of furfurol with pyruvic acid in the presence of glacial acetic acid; *furalphenylacetic acid*, $C_4H_3O.CH=C<^{C_6H_5}_{COOH}$ in silky needles; the *piperide* of this acid $C_4H_3O.CH=C<^{C_6H_5}_{CON.C_5H_{10}}$. He has also prepared *furfuracrolein-acetophenone*,—

$$C_4H_3O.CH=CH.CH=CH.CO.C_6H_5,$$

which crystallises in dilute alcohol in needles fusible at 52—53°; *furfuracrolein-acetic acid*, in needles of a faint yellow colour melting at 153—154°; and finally, *semicarbazide of furfuracrolein*, prepared by dissolving 2 grms. of furfuracrolein in water and adding 2 grms. of hydrochlorate of semicarbazide and 2 grms. of acetate of potassium; it crystallises in alcohol and melts at 215—219°.

Products of the Reaction of Formic Aldehyd on Gallic Acid.—R. Möhlau and L. Kahl.—By this reaction the authors have succeeded in isolating a substance by heating a mixture of 2 molecules of gallic acid and 1 molecule of formic aldehyd with fifteen times the quantity of dilute hydrochloric acid (1 : 5). The substance is a crystallised methylene-digallic acid, difficultly soluble, of which the anhydride, $C_{15}H_{10}O_9$, has been analysed, and probably corresponds to the following constitutional formula—



This acid dissolves in concentrated sulphuric acid with a yellow colour, turning a cherry red by the action of nitric acid; its alkaline solution takes a red colour when exposed to the air.

On Formaldehyd-trioxyfluorone-dicarbonic Acid.—R. Möhlau and L. Kahl.—If we dissolve methylene-digallic acid in concentrated sulphuric acid and heat slowly, the yellow solution takes a green colour at about 50°, then an intense blue; the acid in question, $C_{15}H_{15}O$, appears in the form of a crystalline violet powder, and constitutes a colouring matter for mordants. The acetyl-derivative melts at 140·5—141·5°, at the same time turning brown; its benzoyl-derivative crystallises in alcohol in colourless prisms melting at 250·5—252·5°. The tetracetyl derivative is in the form of brilliant flakes melting at 241°.

The Final Product of the Action of Chloride of Nitrogen on Dimethylaniline.—W. Hentschel.—The author has previously obtained a compound, $C_{24}H_{13}Cl_{19}N_2$, by this method. He now finds that he can obtain the same body more easily by saturating a 30 per cent solution of dimethylaniline in benzene, first with hydrochloric acid, then with chlorine, and finally with an excess of chloride of nitrogen, keeping the whole for some hours away from the light. The crystalline mass thus formed is freed from the ammonium compounds by washing with water, and the aqueous solution is shaken up with benzene, which, on being left, gives a crystalline salt on evaporation. The purified product melts at 117°.

Synthesis of the Naphthindol Derivatives.—O. Hinsberg and A. Simcoff.—The easy formation of indolsulphonic acids according to the equation—

$$ONaSO_2>HO>CH-CH<^{OH}_{SO_2ONa}+C_{10}H_7.NH_2=$$
$$=NaHSO_3+2H_2O+C_{10}H_6<^{NH}_{CH}>CSO_3Na$$

induced the authors to experiment on β-naphthindolsulphonic acid, and in the endeavour to transform it into the principal derivatives of the series β-naphthindol. They here describe the methods adopted by means of which they have prepared several of these bodies.

MISCELLANEOUS.

Messrs. John J. Griffin & Sons.—Notice of Removal.—This old-established firm have recently removed from their premises at 22, Garrick Street, Covent Garden, into buildings which have been specially constructed for their work, at 20-26, Sardinia Street, Lincoln's Inn Fields. This has been rendered necessary owing to increasing work, which has demanded larger and more adapted buildings, the workshops in Sardinia Street being considerably extended.

Royal Institution.—The Christmas Course of Lectures, specially adapted to young people, at the Royal Institution, will be delivered this year by Sir Robert Stawell Ball, LL.D., F.R.S., Lowndean Professor of Astronomy and Geometry in the University of Cambridge. The subject will be "Astronomy," and the lectures (which will be illustrated by models and the optical lantern) will deal with the sun, the moon, the inner planets, the great planets, shooting stars, and new methods. The first lecture will be delivered on Tuesday, December 27th, at 3 o'clock, and the remaining lectures on December 29th and 31st, 1898, and on January 3rd, 5th, and 7th, 1899.

The Edinburgh University Chemical Society met on November 14th, when Prof. Crum Brown delivered the Presidential Address. Prof, Crum Brown gave a short sketch of Kolbe's life, and reviewed his work under the following heads:—Sulphone Acids; Joint Work with Frankland on the Nitriles; Relation of the Alcohols, Aldehyds, Acids, and Ketones to one another; Electrolysis of Organic Salts; Oxyacids. He specially pointed out the remarkable originality and independence of Kolbe's work and speculation, and their bearing on modern theories of chemical constitution.

International Exhibition of Electricity.—An International Exhibition of Electricity and the Silk Industry will be held at Como in 1899, to celebrate the centenary of Volta's great discovery, Como being his native city. In this Exhibition the history of a century in the vast field of electricity will be reviewed, and a congress of electricians will discourse on the most recent progress of the science. The silk industry is a trade much developed in Como, and it is considered that it would be interesting to show the application of electric energy to an important series of machine tools. Scientific men and engineers from all parts of the world will, it is hoped, take part in the Congress. The Exhibition will be divided into twelve sections, besides the Honours class.

Electrolysis of Bromides and Alkaline Fluorides.—H. Pauli.—The author has repeated, on the bromides and alkaline fluorides, Œttel's experiments on the chlorides. The law for the formation of hypobromides and bromates appears to be sensibly the same as that which regulates the formation of the hypochlorites and chlorates. On the other hand, the electrolysis of the alkaline fluorides has not given any oxygenated salts. The solution after electrolysis contains peroxide of hydrogen, formed according to the equation—

$$Fl_2 + 2KHO = 2KFl + H_2O_2.$$

The presence of peroxide of hydrogen was recognised by the ether and chromic acid reaction.—*Zeit. für Electrochemie*, 1898, No. III., p. 474.

MEETINGS FOR THE WEEK.

MONDAY, 28th.—Society of Arts, 8, (Cantor Lectures). "Acetylene," by Prof. Vivian B. Lewes.

WEDNESDAY, 30th.—Society of Arts, 8. "Photographic Developers and Development," by C. H. Bothamley, F.R.S.

THURSDAY, Dec. 1st.—Chemical, 8. "Oxidation of Polyhydric Alcohols in presence of Iron," by H. J. H. Fenton, M.A., and H. Jackson, B.A., B.Sc. Ballot for the Election of Fellows.

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THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2036.

RUTHENIUM TETROXIDE: AN EXPLOSION.

By JAS. LEWIS HOWE.

IT may be worth while to call attention to an explosion which occurred recently in this laboratory in connection with work on ruthenium tetroxide. As is well known, the only satisfactory method of obtaining pure ruthenium is that of passing a rapid current of chlorine through a solution of the melt obtained by fusing crude ruthenium with caustic potash and saltpetre. The distillate, which consists of RuO_4, is generally received in dilute alcoholic potash, the ruthenium being precipitated as a hydroxide. In the case noted the distillate was collected in a small flask for the purpose of obtaining the RuO_4, the excess of chlorine and RuO_4 being led into dilute alcoholic potash, the amount of alcohol being about 10 per cent. After some 5 grms. of RuO_4 had been collected the chlorine tube became stopped up, and the alcoholic potash solution sucked back into the flask containing the RuO_4. In a moment there was a very violent explosion, the apparatus being completely shattered. The force of the explosion can be judged by the fact that a splinter of the thin flask was driven through a thick glass bottle standing near by, making a hole about 3×1 m.m., but not breaking and hardly cracking the bottle. One is reminded of the accident in Deville's laboratory, when nearly 100 grms. of RuO_4 in process of distillation exploded with terrific violence. RuO_4 is so rapidly reduced by organic substances that, if any considerable quantity is present, the heat of the reaction causes instantaneous decomposition. A drop of RuO_4 coming in contact with rubber, wood, or many other organic substances, instantly explodes. On the other hand, in the distillation with chlorine, the RuO_4 can be received apparently with perfect safety in dilute alcoholic potash.

The dense black smoke produced when RuO_4 explodes is readily soluble in hydrochloric acid, and hence probably consists of Ru_2O_3. When RuO_4 in a liquid condition is brought in contact with a lump of sulphur, the latter becomes gradually covered with a black deposit, and in the course of a few moments an explosion takes place. Here the sulphur seems capable of reducing RuO_4, a fact hitherto unnoticed.

Chemical Laboratory of the Washington and Lee University, Lexington, Virginia.

NOVEL PRODUCTION OF VORTEX MOTION.

By C. S. STANFORD WEBSTER, F.I.C., F.C.S.

WHEN the freshly gathered leaves of the native Eucalyptus tree (*Eucalyptus globulus*) are ignited. they project vortex rings in considerable numbers in succession, accompanied by a spluttering noise. The best results are obtained by holding the scythe-shaped leaf vertically and igniting the apex,—this being the part where the greatest number of translations are obtained. The leaves experimented upon were some very fine specimens of San Remo production.

Possibly in the production of these vortex rings, blisters are first formed by the extrusion of the cuticular tissues, and, on the blisters bursting, air or aqueous vapour is spontaneously liberated, the rings being rendered visible on their contact with the smoke from the burning external portion of the leaf. The leaves of the small English variety of *Eucalyptus* possess similar properties to the native product, but in a lesser degree, the rings projected being insignificant in size, comparatively speaking.

It is of course quite immaterial in the production of vortex rings whether the smoke or vapour be inside or outside the apparatus, as can easily be demonstrated by placing an empty Tait's apparatus (this consists of a box with a large round hole at one end, the other extremity being covered with a tense sheet of caoutchouc) suddenly in front of a dense cloud of ammonium chloride vapour, and striking the caoutchouc sheet at the same moment,—a vortex ring is formed, being rendered visible after its translation through the vapour.

The author uses the vapour obtained by heating the solid ammonium chloride, in preference to the usual method in which the two constituents are placed side by side, since the vapour thus obtained is not only denser, and more agreeable to work with, but can be kept under complete control.

If desired to fill the Tait's apparatus with the vapour, the solid is heated in a wide glass tube, one end of which is connected directly with the box by means of caoutchouc tubing, and to the other end a narrow glass tube is attached, and bent back parallel with the volatilising tube, so that the same flame heats both simultaneously; this narrow tube then terminates in a long caoutchouc tube used for blowing into. By gently blowing into the glass apparatus the respired air is heated, and at the same time drives the volatilising ammonium chloride into the box, which is quickly filled with the vapour.

POTASSIUM FERRO- AND FERRICYANIDES AS REAGENTS.

By ROBERT MELDRUM, F.C.S.

Molybdenum.

$K_3Fe(CN)_6$, no result with acid or alkaline solutions, even on boiling.

$K_4Fe(CN)_6$, with acid solutions deep brown colour, discharged to a colourless solution by NH_4HO. This test is reliable to the extent of 1 in 50,000, and is very characteristic. AsH_2S gives with 1 in 50,000 a decided brown colouration; Zn+HCl, no result; Zn+HCl+KCNS, a red colouration; it will be seen that the reagent is a delicate one. With neutral solutions, on boiling a dirty green precipitate results, which on adding NH_4HO drop by drop is turned blue, and is latterly dissolved to a yellowish green opalescent solution on the addition of more alkali. Reliable to the extent of 1 in 400, though a precipitate results on boiling with a much weaker solution than this. Either reagent is preferable to sodium hydrogen phosphate.

Cadmium.

$K_4Fe(CN)_6$, white precipitate; unchanged on boiling, soluble in NH_4HO, insoluble in dilute acids.

$K_3Fe(CN)_6$, yellow precipitate; unchanged by boiling, soluble in NH_4HO or HCl, insoluble in H_2SO_4 or acetic acid. The ferricyanide is the more delicate and distinct of the two tests, the precipitate of which, in solutions containing less than than 1 in 2000, appears white. This I find to be a useful reagent for cadmium salts, and consider it superior to H_2S.

Silver.

$K_3Fe(CN)_6$, brick-red precipitate, changing to dirty yellow colour on boiling, soluble in NH_4HO, but insoluble in HNO_3.

$K_4Fe(CN)_6$, white precipitate, unchanged by NH_4HO; turned green by boiling, which is turned brown by NH_4HO. The precipitates are not soluble in excess of reagent. Reliable only for strengths up to 1 in 400.

Gold.

$K_4Fe(CN)_6$, no result in cold; but on boiling yields green colouration, discharged by NH_4HO and forming a yellow precipitate, partly soluble in excess to a yellow solution.

$K_3Fe(CN)_6$, no result till on adding few drops of NH_4HO, when dirty yellow precipitate forms, insoluble in excess. Not reliable for solutions weaker than 1 in 300, and, therefore, is not so useful as the ordinary tests.

Platinum.

$K_3Fe(CN)_6$, no result with acid or alkaline solutions, even on boiling.

$K_4Fe(CN_6)$, with 1 per cent solution gives heavy crystalline precipitate, forming a dark green liquid on boiling; turned black by NH_4HO. A few drops of the reagent added to a 0·2 per cent solution and boiled produces very dark green solution, appearing almost black. On boiling with excess of reagent a light green precipitate results, which NH_4HO turns olive-green, then yellow, and as more $K_4Fe(CN)_6$ is added forms a yellow solution. The green precipitate is soluble in HCl, forming a very strong indigo-blue liquid: by this means less than 1 in 5000 may be detected. The other tests are good for 1 in 1000. These reactions have been found of some use in qualitative work.

Mercury.

Mercuric Salts.—$K_3Fe(CN)_6$ gives no result in cold solutions, but on boiling a dark green solution is formed, which on dilution and addition of NH_4HO throws down dirty yellow precipitate.

$K_4Fe(CN)_6$, a white precipitate, soluble in excess; on adding more reagent it becomes a pale yellow, and on heating turns to a brilliant green, which NH_4HO changes to a flesh-colour. These tests hold good for solutions of 0·25 per cent strength. None of them are so delicate and useful as KI.

Mercurous Salts.—$K_3Fe(CN)_6$, light brown precipitate; turned green by boiling, and on adding NH_4HO yellow.

$K_4Fe(CN)_6$, white precipitate; changing to grey on boiling, and black by NH_4HO. These reactions are distinct with 0·25 per cent solutions.

Lead.

$K_3Fe(CN)_6$, no precipitate; on adding NH_4HO yields dirty yellow precipitate, which on boiling becomes pale yellow.

$K_4Fe(CN)_6$, white precipitate; not changed by boiling or NH_4HO, insoluble in acetic acid. Both reliable for 0·2 per cent solutions of lead acetate.

Zinc.

$K_4Fe(CN)_6$, white precipitate; insoluble in HCl, or NH_4Cl, or NH_4HO.

$K_3Fe(CN)_6$, yellow "ochre" precipitate; soluble in NH_4HO, also in hot HCl. This is a most useful and satisfactory reagent for zinc, as the usual reagents, NH_4HO, $(NH_4)_2S$, NaHO, Na_2CO_3, and KCN, all yield white precipitate, and hence Al, which gives no precipitate with $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$, is much easier distinguished from Zn by this means.

The Examination of Blood Stains.—We are requested to state that at the meeting of the Society of Public Analysts to be held on Wednesday Evening next, December 7th, an illustrated lecture will be delivered by Mr. A. H. Allen, F.I.C., of Sheffield, on "The Use of the Micro-Spectroscope, and the Methods of Detecting Blood in Chemical-Legal Investigations." Any persons who may be interested in the subject are invited by the Council to attend. Intending visitors who will not be introduced by members of the Society are requested to apply for tickets to Mr. E. J. Bevan, Hon. Secretary, 4, New Court, Lincoln's Inn, London, W.C.

LABORATORY NOTES.

By WM. FRENCH, M.A., F.I.C.

Equivalents of Metals.

In comparing the equivalents of some metals with that of oxygen (by conversion to oxide) for class work, I have adopted the following method, which I find is easily performed and possesses none of the difficulties of loss by "spurting," &c., with the advantage that, as a rule, the whole class can obtain fairly concordant results.

About 1 grm. of metal (copper, tin, &c.) is placed in a hard glass test-tube (6" × ¾") which is loosely closed with recently ignited asbestos fibre, and weighed. The plug is carefully removed, sufficient nitric acid is added to dissolve the metal, and the plug replaced. The tube is now placed on a sand-bath, sloping at about an angle of 30°, and heated to remove excess of acid. When dry, the tube is strongly heated over a naked flame, taking care to heat the whole of the tube in turn. Cool, re-weigh, and calculate in the usual way. A glass-wool plug will also do.

Working with a class of twelve students, as a mean of ten results the number 31·91 was obtained for the equivalent of copper, the whole of them being very near to that number. For tin the results have been equally concordant, but not quite so near to the number obtained by a more accurate method.

Possibly this method is in use, but it certainly is not common, and I would recommend those who have not tried it as a class experiment to do so in preference to the usual crucible or inverted funnel method so generally figuring in the text-books.

Bury Grammar School.

ON THE DISSOCIATION SPECTRA OF MELTED SALTS.

METALLOIDS: CARBON.

By A. DE GRAMONT.

As with the metalloids already described, it is difficult to obtain the carbon lines in melted salts. But if the melted carbonated salt is taken out of the flame, the carbon lines appear, as do also the air lines, and their brightness appears to increase with the length of the spark—that is to say, with the increase of the difference of potential. Being desirous, however, of keeping the spark on the melted salt very short, so as to do away with—or diminish—the air spectrum, I intercalated in the secondary circuit of the coil an exciter with an adjustable attachment, to enable me to establish a sufficient difference of potential in the discharge from the condenser (which was formed of a variable number of Leyden jars).

By keeping the melted salt in a pasty state of fusion, a little above the flame, we can see the appearance of the spectrum of the carbon lines in a very distinct manner. I have compared it with that of free carbon, either in Siberian graphite and in retort carbon; this latter, however, even after treatment with acids, continued to give numerous other lines, due to impurities (Ca, Ba, Fe, &c.).

The Siberian graphite from the Alibert mines, on the contrary, gave only the carbon spectrum, the spectrum of the lines and bands of Swan mixed together, as well in perfectly dry air and carbonic acid as in pure hydrogen. But I have never found a trace of the Swan bands in the melted salts, where the carbon lines only were associated with those of the metal. It appeared to me important to make observations of a band spectrum, associated with a line spectrum, under electrical conditions, where, up to the present, spectra of dissociation only remained.

Below are given the carbon lines I obtained with the carbonates, placed in accord with the observations of previous experimenters with free carbon (see Table).

So as to be quite certain as to the origin of the lines,

	Free Carbon.				*Melted Carbonates.*		
	Angström and Thalén.	*i.*	Eder and Valenta.	*i.*	A. de Gramont.	*i.*	
C α. ..	658·40	10	658·42	1	—		Not seen.
	657·85	12	657·87	1	657·85	7	Very distinct.
	569·51	6			—		Not seen.
Group I.	566·19	6	Not photographed.		566·22	3	Easily seen.
	564·75	8			564·86	3	,,
	563·96	2			564·10	2·5	,,
	538·0	2	539·98	2	537·99	5	Fairly well seen.
	515·14	5	516·12	1	515·16	7	Very distinct.
Group II.	514·50	6	514·49	1	514·46	7	,,
	513·38	3	513·37	1	513·29	7	,,
	Not seen.		455·63	1	—		Not seen.
C β ..	426·66	10	426·75	4	426·70	9	Strong, wide, very diffuse.

I made observations in pure hydrogen with the condenser spark on carbonates of lithium and potassium melted on a platnium spiral made incandescent by means of an electric current, thus operating in an atmosphere entirely free from all carbonated gases. I felt, however, sure that in the previous experiments the spark above the Bunsen burner did not give any carbon lines beyond those in the carbonate.

The values given in the accompanying table have been corrected to the normal spectrum of Rowland. The results given by MM. Eder and Valenta were obtained by photography. The intensities, *i*, are reckoned for 12= maximum.

The double line C α is generally given of the first importance; but its origin appears to be doubtful to MM. Eder and Valenta. On the other hand, several writers, using only a slight dispersion, have mistaken the least refrangible line of hydrogen, H α 657·3 (C of Frauenhofer), of which it is difficult to get rid, as one of its components. I therefore studied this part of the spectrum with most particular care, making use of a spectroscope with four prisms, on Thalén's principle, having great dispersive power. But whether with pure carbon or with melted carbonates, this instrument only enabled me to see one line, very well marked and slightly diffused, but not doubled. It corresponds very well to the most refrangible line of the so-called double one of Angström. I found for it a definite position, 657·85, taking as data H α 657·30 (Ames) and Li 670·82 (Kayser and Runge). The position of the three lines was measured in the same spectrum in turns and fractions of a turn of the micrometer screw of the apparatus. On the other hand, I have never been able to find the line 658·4 with pure carbon, in various pure and dry gaseous surroundings, or by varying the conditions of the experiment. I therefore consider it as not belonging to carbon.

Group I. is not very intense, but the line 537·99 and Group II. are strong and brilliant. The wide line in the indigo, C β 426·70, is the strongest and most characteristic of carbon. Increasing the condensation widens it enormously, even transforming it into a nebulous band.

All these lines have been observed, not only in alkaline carbonates, but in cyanides, sulphocyanides, and even in sulphocarbonates when below their temperatures of decomposition. I have even observed C α, C β, and Group II. by making a condenser spark strike between two solid beads of K_2CO_3 on two platinum wires.

Finally, I have observed in free carbon, in various gaseous media, a very well marked red line (609·70) the origin of which appears to be uncertain, for it is absent in the dissociation spectra of the carbonates, though its presence is incontestable in graphite, where no line foreign to carbon has yet been found.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 13.

Appointment.—Mr. E. H. Todd, a Matriculated Student at the South-Western Polytechnic Day College for Men, has been appointed to an open Exhibition in Physics and Chemistry at Christ Church, Oxford, of the value of £80 per annum, tenable for four years.

THE ESTIMATION OF BORIC ACID.

By M. VANDAM.

KLEIN has already studied the action of mannite on boric acid, and has noted the formation of a body giving an acid reaction with litmus paper; he also found an analogous property to this with glycerin, erythrite, dextrose, levulose, and the galactoses. Quercite and the polyglucocides behave in a different manner.

Lambert taking up the question, noticed that the property of forming acids in conjunction with boric acid belonged to the primary polyatomic alcohols.

Barthe proposed a method for the estimation of boric acid and borates, in which he made use of the associated acid body obtained by the addition of an excess of glycerin to the boric solution, and titrating with a solution of decinormal soda in the presence of sensitive litmus or phenolphthalein.

The number of c.c. of normal soda multiplied by 0·0062 gives by weight the amount of boric acid contained in the sample (0·0062 being the equivalent of BoO_3H_3),

In such an estimation I have substituted mannite for glycerin. With mannite the end of the reaction comes gradually, and the last drop of the titrated alkaline solution produces the blue colour perfectly and sharply; while with glycerin, even from the commencement of the operation, there is a persistent violet tint, the precise end of the reaction is more difficult to observe, and it is not at all easy to avoid making a noticeable error in two consecutive experiments.

For a long time past we have been successfully using this property of mannite in testing for and estimating boric acid in butters; we have made more than a hundred comparative examinations.

Testing for and Estimating Boric Acid in Butters.

1. Fifty grms. of butter are well washed with 20 c.c. of warm water.

2. The washings, nearly always acid, are saturated with a few drops of decinormal soda in the presence of sensitive litmus.

3. The blue liquid is divided into two test-tubes.

4. To one of these test-tubes we add 1 or 2 grms. of mannite, the other tube serves as a check.

In the presence of boric acid the tube containing mannite takes an intensely red colour.

With this solution we carry out the estimation by the use of decinormal soda, until the sudden appearance of the blue colour, when the number of c.c. of decinormal soda multiplied by 0·0062 will represent the weight of the boric acid contained in the sample.

The theory of these associated acid bodies is far from being clearly established. The following conclusions result from our researches:—

It is a fact that the addition of an excess of one of the polyatomic alcohols to a known weight of boric acid gives an acidity which is shown most distinctly by the aid of litmus, and that this acidity corresponds exactly to the volume of the decinormal solution of soda. Now, it seems

evident that, since we can reciprocally substitute a hexatomic alcohol for a triatomic alcohol without interfering with the estimation as far as the calculations go, we estimate in this case, not the associated acid body, but only the boric acid taken progressively from its alcoholic combination by the soda of the titrated solution up to the moment when the polyatomic alcohol, completely free from its boric combination, remains inert, when the slightest excess of soda instantly produces the blue colour.—*Journ. de Pharm. et de Chim.*, Series 6, vol. viii., No. 3.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 3rd, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

(Concluded from p. 264).

129. "*The Yellow Colouring-matters of Rhus Cotinus and Rhus rhodanthema.* Part VI. By ARTHUR GEORGE PERKIN.

Venetian sumach, the leaves of *R. Cotinus*, contains myricetin, and not quercetin as stated by Löwe (*Zeit. Anal. Chem.*, 1874, xii., 127). The leaves of *R. rhodanthema*, the yellow cedar of New South Wales, contain quercetin and gallotannic acid. The stems of both plants contain ficetin, and the leaves thus contain the more highly oxidised colouring-matters, as quercetin and myricetin are considered to be hydroxy- and dihydroxy-fisetin respectively. Other members of the *Rhus* family hitherto examined contain no fisetin in the stem. The Venetian sumach examined contained 16·7 per cent, and the *R. rhodanthema* leaves 9·5 per cent of tannin.

The leaves of *Artocarpus integrifolia* (Jackwood tree), *A. incisa* (bread fruit), and *A. lakoocha* are devoid of colouring-matter.

130. "*Colouring-matters of the New Zealand Dyewood 'Puriri.'*" By ARTHUR GEORGE PERKIN.

"Puriri" (*Vitex littoralis*) is a large tree, growing in northern New Zealand, and chiefly used for building and similar purposes. Its tinctorial properties are little known. It contains two colouring-matters in the form of glucosides.

Vitexin, $C_{15}H_{14}O_7$ or $C_{17}H_{16}O_8$, the chief product, is a canary-yellow crystalline powder, distinguished by its sparing solubility in most solvents. Owing to the difficulty of obtaining substitution products without decomposition, its molecular weight is at present uncertain. *Acetylvitexin*, $C_{15}H_9O_7Ac_5$ or $C_{17}H_{10}O_8Ac_6$, forms colourless needles melting at 251—256°. On fusion with alkali, phloroglucinol, acetic and parahydroxybenzoic acids are formed, whilst boiling aqueous or alcoholic potash solutions give phloroglucinol and parahydroxyacetophenone. Further, the product of the ethylation of vitexin with boiling alcoholic potash yields paraethoxybenzaldehyde, paraethoxybenzoic acid, and a phloroglucinol derivative. Warm nitric acid (sp. gr, 1·54) forms metadinitroparahydroxybenzoic and picric acids, but when dilute acid is employed a sparingly soluble *nitro*-compound,—

$$C_{15}H_6O_5(NO_2)_4,$$

of unknown constitution, is also obtained in small quantity. This consists of small lemon-yellow needles, which dye mordanted calico; it is converted by strong nitric acid into picric acid, and appears to be closely related to vitexin. With nitrobenzene it forms an addition product, $C_{15}H_6O_5(NO_2)_4,C_6H_5NO_2$, crystallising in orange-coloured needles which lose nitrobenzene at 150°, or by digestion with alcohol. Vitexin gives very pure yellow shades on calico mordanted with chromium and aluminium salts, but owing to its insolubility these are of a poor character. They somewhat resemble the corresponding shades given by apigenin, and, as the chief decomposition products of both colouring-matters are identical, it is probable that apigenin and vitexin are closely related.

Homovitexin, $C_{16}H_{16}O_7$ or $C_{18}H_{18}O_8$, is present in the wood only in minute quantity. It crystallises in fine primrose-yellow needles, melts at 245—246°, and is distinguished from vitexin, which it otherwise resembles, by its ready solubility in alcohol. Fusion with alkali gives phloroglucinol and parahydroxybenzoic acid, and treatment with dilute nitric acid yields metadinitroparahydroxybenzoic acid. It dyes mordanted fabrics feebly.

The shades given by "puriri" with chromium and aluminium mordants are distinguished by their pure yellow tone, and may have some commercial utility.

131. "*Cannabinol.*" By T. B. WOOD, M.A., W. T. N. SPIVEY, M.A., and T. H. EASTERFIELD, M.A., Ph.D.

In former communications (*Proc.*, 1898, xiv., 66, 153) a number of derivatives of cannabinol have been described; a detailed account of these is given in the present paper. The oily lactone (*loc. cit.*, 153), prepared from nitrocannabinolactone (oxycannabin), is shown to be a metatolylbutyrolactone, oxycannabin being the corresponding nitro-derivative. By the oxidation of cannabinolactone, a lactonic acid is produced, which on fusion with potash yields isophthalic acid.

Nitrocannabinolactonic acid is obtained by oxidising oxycannabin either by dilute nitric acid in a sealed tube or by potassium permanganate.

The volatile fatty acids produced on oxidising cannabinol by nitric acid are shown to be normal butyric (Dunstan and Henry, *Proc.*, 1898, xiv., 44), normal valeric, and normal caproic acids, valeric acid being formed in the largest amount.

132. "*Derivatives of Hesperitin.*" By A. G. PERKIN.

Hesperitin is found as the glucoside hesperidin in the citron, bitter orange, and other fruits of the same class. With potassium hydrate solution at 100° it gives phloroglucinol and hesperitinic or hydroxymethoxycinnamic acid. It thus appears to have the constitution—

$$OH\cdot C_6H_3(OMe)\cdot CH:CH\cdot CO\cdot O\cdot C_6H_3(OH)_2$$

(Hoffmann, *Ber.*, 1876, ix., 685; Tiemann and Will, *Ber.*, 1881, xiv., 948). With alcoholic potassium and sodium acetates, hesperitin gives the compounds—

$$(C_{16}H_{14}O_6)_2,KC_2H_3O_2, \text{ and } (C_{16}H_{14}O_6)_2,NaC_2H_3O_2,$$

which form colourless needles and decompose on treatment with boiling water, regenerating hesperitin. With sodium and potassium bicarbonates, *sodium hesperitin*, $C_{32}H_{27}O_{12}Na$, and *potassium hesperitin*, $C_{32}H_{27}O_{12}K$, are obtained, crystallising in minute colourless plates. The formula of hesperitin is thus $C_{32}H_{28}O_{12}$.

Azobenzenehesperitin, $C_{32}H_{24}O_{12}(N_2Ph)_4$, forms red needles, melts at 246—247°, and yields a *diacetyl* derivative, $C_{32}H_{22}O_{12}Ac_2(N_2Ph)_4$, crystallising in ochre needles melting at 240—242°. Hesperitin should thus contain six hydroxyl groups, and this view of its constitution is confirmed by the formation of *acetylhesperitin*, $C_{32}H_{22}O_6Ac_6$, which crystallises in colourless needles melting at 127—129°.

If hesperitin were $C_{16}H_{14}O_6$, the constitution assigned by Tiemann and Will would thus be correct. Though not considered to be a polymeride of a substance of this formula, it must consist of two very similar groups linked together, as Hoffmann (*loc. cit.*) obtained from hesperitin a nearly quantitative yield of phloroglucinol and hesperitinic acid.

Research Fund.

A meeting of the Research Fund Committee will be held in December. Applications for grants, accompanied by full particulars, should be received by the Secretaries not later than December 5th. Forms of application can be obtained from the Assistant-Secretary, Chemical Society, Burlington House, W.

THE BANQUET TO PAST PRESIDENTS.

The Banquet to the Past Presidents who have been Fellows for half a century:—

	Elected.	President.
Gilbert, Sir Joseph Henry, F.R.S.	May 18, 1841 ..	1882-83
Frankland, Sir Edward, K.C.B., F.R.S.	December 20, 1847	1871-73
Odling, William, M.B., F.R.S.	January 17, 1848	1873-75
Abel, Sir Frederick Augustus, Bart., K.C.B., F.R.S.	March 21, 1848 ..	1875-77
Williamson, Alexander William, LL.D., F.R.S.	May 15, 1848 ..	1863 65 1869-71
Gladstone, John Hall, Ph.D., F.R.S...	December 18, 1848	1877-79

was held at the Whitehall Rooms, Hôtel Métropole, on Friday November 11th, 1898, Professor JAMES DEWAR, F.R.S., President, in the Chair.

After the toasts of the Queen and the Prince and Princess of Wales, the PRESIDENT said:—

"I have now the honour to propose to you what you must all regard as a toast to which I cannot possibly do justice, the health of six of the most distinguished Past Presidents of the Chemical Society who for more than half a century have been members of that body. It is admitted on all hands that Chemical Science has added enormously to the resources and power of mankind, and that its successful cultivation involves the exercise of every faculty of the human mind. We have here six illustrious examples of successful scientific culture, and, I would add, of bracing moral influence,—men whose one idea it has been, with steady aim and vigilant eye, to labour on with that sole incentive of scientific work, the triumphant hope of making an advance. These men have laboured for half a century in our interests, and they have added enormously to our knowledge of the science. It is almost impossible to realise the variety of the work they have done; the width of it is something appalling; when I tell you that, amongst them, they have recorded upwards of four hundred and fifty separate communications—how many there are that have not been recorded I cannot say—and that among these four hundred and fifty there are many papers of the highest importance, I am sure you will agree with me that they have exercised a remarkable influence on the development of our science. It was well that the Chemical Society of London—the oldest Chemical Society in the world—should inaugurate this banquet. The Council felt that probably they might never again have the opportunity of calling together such a distinguished body of men as they have the honour of offering this banquet to to-night. We are still able to go back to a man, who sits on my right hand, who worked in the laboratory of Thomas Thomson, who has seen Dalton and the beginning of the Atomic Theory, probably the most wonderful of all the laws of Nature which man has ever been permitted to decipher. That being the case, the way in which the idea has been received by all the chemists of this country is apparent from the number of men of talent and the variety of classes here to-night. Bnt beyond that, the sympathy of every chemist in the world is with us to-night at this banquet. The large number of congratulatory telegrams and communications that we have received to-day from every country where the science of chemistry is cultivated, will give some idea of the appreciation with which this banquet is regarded throughout the whole civilised world. We have received communications from France, Holland, Belgium, Germany, Sweden, Russia, Austria, the United States, and other countries. It is unnecessary for me to read every name, for every man identified with the progress of chemistry in every civilised country has responded by sending some form of congratulation. In every case they write as if they were present with us, as you will understand from the few illustrations I will give you of the sympathetic language they use. Professor Friedel writes:—'I should have been happy to associate myself with the Chemical Society in doing honour to these veterans of science. I have the honour to be the friend of most of them, and the beneficent action they have exerted on Chemical Science cannot be esteemed too highly. They form the finest phalanx of the Fathers of our science which exists in any country. With these sentiments, you will understand the liveliness of my regret to be able to take part from afar and in spirit only in the honour paid them.' We have also received congratulations from learned societies both in Germany and Russia. At a meeting of the Russian Chemical Society the following resolution was passed:—'That the Society avail itself of the exceptional opportunity of being able to congratulate conjointly Sir Joseph Henry Gilbert, Sir Edward Frankland, Professor Odling, Sir F. A. Abel, Dr. A. W. Williamson, and Dr. J. H. Gladstone, whose distinguished services during half a century stand out as a model for all investigators in chemical science, and also express the wish to see the further results of their labours in the annals of science for many years to come.' The telegram from the German Chemical Society strikes me as very happy. Dr. Liebermann says:—'The sister Society sends both Jubilee congratulations and greetings to the Jubilee celebration of the Presidents of the Chemical Society, Gilbert, Frankland, Odling, Abel, Williamson, and Gladstone.' This shows, I think, that our Continental brethren appreciate the honour we desire to offer these distinguished men; and we need not be surprised that there is something more throughout these communications than mere cosmopolitanism in science. They breathe the spirit of friendly regard, of reverence, and even of love towards men who have done so much to advance the common cause of our science. How impossible it seems to sum up in any short speech the work that these men have done! If I attempted to classify them, I should say that if we regarded them as twos and twos they would not group well together, but if we take three at a time they bear somewhat close relations one towards another. I would say that Gilbert and Abel and Gladstone are monarchs of dependent kingdoms, whereas Frankland and Odling and Williamson are a triumvirate that have legislated towards the imperial side of chemical science.

"The work of Gilbert, as we know, was early differentiated into that most complex and mysterious study, the study of organic life. For the last fifty years he has devoted his attention to the physiology of plant life in every phase of its development. With a skill that has been unprecedented, he has recorded from year to year the variations in the growth of every kind of nutritious plant. He has examined into the meteorological conditions, the variations of climate, of soil and of mineral agents, of drainage, and of every conceivable thing affecting the production and development of plant growth. These memoirs are admitted throughout the world to be unique in their importance. Wherever the chemist or the physiologist, the statistician or the economist, has to deal with these problems, he must turn to the results of the Rothamsted experiments in order to understand the position of the science of our time. These results will be for ever memorable: they are unique and characteristic of the indomitable perseverance and energy of our venerated President, Sir Henry Gilbert.

"The next among them, Sir Edward Frankland, I should characterise as one of the most remarkable experimentalists of this or any other age. He has been gifted with an absolutely unique faculty for experimental work and observation. The breadth and variety of his work is positively astounding. From early times devoted to the study of Organic Chemistry, he has branched out not only into Mineral Chemistry, but every form almost of applied industry. His early work on the organo-metallic bodies, so fertile in the way of future development, will be ever

memorable. These bodies have been the means of adding to our knowledge of synthetical substances produced in the laboratory in a way that no other agencies have operated. Along with this work, he has executed investigations bearing on flame and the character of the light emitted by various bodies, and on a large number of questions connected with sanitary chemistry. His great work on the water supply of the United Kingdom, on the sewage question, and other industrial problems, are generally acknowledged to be of great value and importance. Whatever work he has done is marked with the stamp of genius.

"The work of Odling has been an essential factor in the development of modern chemistry. It is characterised by precise and clear ideas, and an almost forensic ability for putting things in a straight, concise, and unembarrassing manner. His early labours in advancing the development of the newer chemistry deserve our warm gratitude, and his many published works and addresses on organic and inorganic chemistry, together with his translation of the work of Laurent, have all been of material service in diffusing a knowledge of our science. The papers he has contributed on Chemical Notation and on the question of types all display a marvellous precision as well as elegance of thought. Every one must admit the debt of gratitude we owe him for his iconoclastic labours in clearing out old and vague notions, and for the courageous manner in which he supported the newer ideas of his time.

"In the case of Abel, we have again a man who, at an early time, had his career differentiated for him. A distinguished student of Hofmann's, his early work was directed to organic chemistry, but he soon diverged into other channels, directing his attention to problems bearing on the chemistry of naval and military matters. We all know his splendid work on gunpowder, guncotton, detonation, and the whole field of explosive agents. Whether in connection with accidents in mines, from petroleum, or from flour, dust, or other agency, Abel has been a marvellous experimenter in the whole field of explosive chemistry. While engaged in these investigations in applied chemistry, however, he was adding to the advancement of pure science by the light which his researches threw upon many questions of chemical theory and by the stimulus thus given to further inquiry. He has had the great satisfaction of living through the age of gunpowder. That body had been the recognised explosive for many hundred years, and I have no doubt that when he commenced his investigations with Noble on gunpowder he never dreamt that he would live to see the day when he would clear out that smoky material and replace it before he left the War Office by a powder that is smokeless. I need hardly tell you that he has also added to our debt of gratitude by the personal services he has rendered to many learned societies.

I come now to Williamson. The work of Williamson proclaims him a truly philosophic chemist. He has had probably the greatest satisfaction of any one I know. He cleared up one of the most intricate and recondite of chemical reactions, that with which we are familiar as etherification, and in so doing he struck at the very root of the chemical problems connected with atomic and molecular weights, and realised and cleared up for ever those mysterious modes of explanation which were undoubtedly faulty and insecure. Before his time, men as great as Berzelius, Mitscherlich, and Graham, believed in that contact or catalytic action which in my early days bridged over the period between the old and the new, and was generally introdnced when no other explanation was forthcoming. Williamson cleared all that away; but the discovery of these ethereal nepenthes did not act in chemistry as they would have done physiologically; they did not produce a soporific effect. They struck at the foundations of our science, and it is to his great credit that he originated advanced ideas, not only as to etherification, but as to molecular weights, type formulæ, and so forth. In fact the chemistry of our time would not be the chemistry of our time but for the work of Williamson. I would further add that he was one of the earliest to introduce the idea of dynamics into chemical science. His suggestion of the dynamical theory of the voltaic battery and of dynamic mobility in apparent stability has been exceedingly fruitful since his time; and if we add to them that most important and original idea of Frankland's, the saturation power of the elementary bodies, we have all the agencies of our modern scientific notions. One other debt of gratitude we owe to Williamson, and that is the interest he took in introducing into this country abstracts of all the important scientific memoirs published on the Continent, It is to him we owe those valuable abstracts which have been printed for many years in the Chemical Society's *Journal*, and have done so much for the advancement of our science.

"Gladstone, on the other hand, represents a type somewhat different from that of any of the others that I have mentioned. He belongs to a characteristically English variety of men who have studied science for its own sake. Like Spottiswoode, De la Rue, and Joule, he has not been a professional scientist in the ordinary sense, but has worked out his long and brilliant scientific career as a labour of patient love. Furthermore, he has created an entirely new department—that which is in modern times regarded as physical chemistry, of which we have here to-night some distinguished representatives. For half a century he has worked on this side of chemistry, for his early investigation of the spectrum of the atmosphere was one of marvellous suggestiveness. He found that the spectrum of Fraünhofer varied at sunset and at sunrise from that at mid-day, and showed that a large number of those absorption lines must originate in the earth's atmosphere. That discovery stimulated further inquiry as to the substance that could produce these lines so characteristic of the solar atmosphere; and later experimenters have found it in the vapour of water and in oxygen. Gladstone's greatest merit, however, lies undoubtedly in his optical researches on the atomic refractions and dispersions of the elements. He has determined the optical constants of hundreds of bodies, and has thus stimulated inquiry in that borderland between physics and chemistry which is so much cultivated in the present day, and the pursuit of which has added so much to our knowledge. He has also contributed largely to miscellaneous inquiries, especially those connected with various voltaic batteries, and other questions conducive to the study of both organic and inorganic chemistry.

"This is but a brief epitome of the work of these great men. It would be, as I have said, hopeless for me to attempt to sum up all their individual labours. We can only skim the surface of the ocean of truth in which they have navigated so well and so successfully. But I will say this: that as experimentalists we are not likely to see their like again, and it is impossible to imagine a more extraordinary galaxy of chemical talent than these six Past-Presidents represent. They have rendered the science of chemistry more glorious for those who strive to follow; and the brilliant record of their discoveries can never be eliminated from the history of our Science. In the future, posterity will regard them as the most gifted and illustrious of the English chemists of the Victorian epoch. My Lords and Gentlemen,—I give you the health of our venerated Past-Presidents, Sir Henry Gilbert, Sir Edward Frankland, Professor Odling, Sir Frederick Abel, Professor Williamson, and Dr. Gladstone."

Sir J. Henry Gilbert—"After the extremely flattering and eloquent terms in which our President has referred to the work of the six Past-Presidents of the Society who are so highly honoured to-night, it is surely a difficult task to say anything in response. I feel that any words of mine would be entirely inadequate; and I must, I think, fall back on what I was intending to say, and give a little personal history of the early times of the Society. You are aware, most of you, that I am to-night in the position of the senior of the Past-Presidents, in consequence of

the death of Lord Playfair. He was, as you know, one of the founders of the Society, and, before he died, the only survivor of those founders. I myself came in within three months of the foundation, and so had some knowledge of the Society's early doings. In fact, before I was really admitted to the Society, under the influence of the late Professor Graham, I undertook the translation of a paper by Redtenbacher and Liebig on 'The Atomic Weight of Carbon'; and that paper occupies eighteen pages in the first volume of the Society's *Memoirs*. I should say that, less than a fortnight ago, I received a letter from Lady Playfair, just before she left to visit her friends in America, in which she said with what interest he had looked forward to being present at the banquet appointed for June—but that was not to be. I first made the acquaintance of Playfair in Liebig's laboratory at Giessen, the year before the establishment of this Society, that is, in 1840. Playfair was at that time very busily occupied in translating the memorable work of Liebig, 'Organic Chemistry in its Applications to Agriculture and Physiology'; and before the session was over he left for this country with Liebig, who was to present the substance of that work as a Report to the British Association at Glasgow in September. You may be interested to know who there were from this country in Liebig's laboratory at that time. Besides Playfair and myself, there were Dr. William Allen Miller, afterwards Professor of Chemistry at King's College; Dr. Stenhouse, who has contributed so much to the *Journal* of this Society; Dr. Angus Smith; and, lastly, Dr. Edward Schunck. He and I are, I believe, the only survivors of that time among those from England who were with Liebig then. Of the Germans who were there, some of the names you will probably remember. There were Heinrich Will, Varrentrapp, Redtenbacher, Hermann Kopp, Scherer, Bromeis, Boeckmann, and others of various nationalities; but I believe that not one of these survives at present. Schunck joined the Society early in 1842, and he from that time to this has devoted himself to scientific investigation. He built a laboratory, and a museum devoted especially to specimens of organic bodies, in his own grounds on the other side of Manchester, where he still lives. He was, in fact, the oldest member of the Society, I believe, except Playfair and myself. He has worked indefatigably ever since; but I am very sorry to say he is not able to be here to-night, having had an attack of bronchitis, which renders it impossible, though it would have given him great pleasure to be present. Referring to that time at Giessen, I may say that Playfair, Stenhouse, and myself, each took our degree then; and Playfair, though joining with us, having gone with Liebig, the responsibility was left with Stenhouse and myself to give the usual supper to the other students of the laboratory, and a few distinguished guests, among whom was Bunsen, who was then at Marburg; and who, I am glad to learn from Sir Henry Roscoe, is still well. Stenhouse was much my senior. We had a large and lively party, but Stenhouse did not enjoy that sort of thing very much, and when the last bottle of champagne was opened, he said: 'Now, Gilbert, I shall leave you to it,' and away he went. That was, however, not near the end of the evening. They stayed a very long time, and we did not exchange the smoky atmosphere of the supper-room for the clearer air outside until early morning. We then went round the boulevards of the little town, the Germans singing students' songs, and coming in time to the hotel where Stenhouse lodged, we serenaded him from the outside. Then someone tried the door, and finding it unfastened, the whole party went up, lighted candles, and serenaded him in bed. Next morning, there was a very capital caricature brought out, showing Stenhouse's rather long nose pointing in one direction, and his longer nightcap in the other. But this is enough of this kind of history, and I must now turn to rather more serious matters. It was in 1843 that I became associated with Mr. (now Sir John) Lawes, in agricultural investigation — a collaboration which has now extended over more than fifty-five years. As you all know, however rude may be some of the methods of the art of agriculture, the investigation of the principles underlying its practices involves a wide range of scientific inquiry. It involves the chemistry of the atmosphere, of the soil, of vegetation, and of animal life and growth. That is to say, besides chemistry, it involves meteorology, botany, vegetable physiology, and animal physiology, to some extent. It is impossible to be a specialist in so many subjects, particularly in these days, and I can only say that in venturing to deal with these other branches of science we have taken great care to avoid mistakes. The wide range of the investigations must be accepted as some explanation of the fact that we have not contributed more of the results to the Chemical Society. Many of them being connected largely with other branches of science, have been recorded in other than purely chemical journals; whilst those having a more directly practical bearing have been published in the *Journal of the Royal Agricultural Society*, or in other agricultural publications—the Rothamsted papers now numbering considerably more than one hundred. But we feel that, however long or short may be the time that we shall still work together, we shall perhaps have done as much in opening up as in solving problems; and that we shall certainly leave plenty for our successors to do. In conclusion, considering that there still remain five of your honoured guests to speak, this is all I will say of my own career, and I will only now ask you, Mr. President, the Council, and the Fellows of the Chemical Society, to believe that I esteem very highly the great honour you have conferred upon me to-night."

Sir Edward Frankland—"Allow me to thank you, Mr. President, and the Council of the Chemical Society for this delightful entertainment which you have prepared for the Past-Presidents who have attained Jubilee rank. It was a generous, unique, and happy idea, which I feel sure we all heartily appreciate, not only as we sit at your hospitable board, but also when we reflect on the kind feelings which led to the conception of that idea. There used to be a phrenological organ entitled 'love of approbation,' and whether there is or is not a part of the brain told off to perform this function, I trust that chemists are not behind the rest of humanity in appreciating such an honour as you have conferred upon us on this auspicious occasion. Nothing could he more agreeable than thus meeting so many colleagues who are worthily keeping up the high reputation of the Chemical Society. There is but one drawback to our enjoyment, and it has been very feelingly alluded to by Sir Henry Gilbert, namely, that one who so recently stood at the head of our Past-Presidents should not still be present amongst us. In the lamented death of Lord Playfair, chemistry and science generally have sustained an immeasurable loss; for he was a binding-link between science and the State, always ready to fight for the cause of truth against prejudice and ignorance, and never ceasing in his efforts to bring home to our rulers the vast importance of the applications of science to the progress, health, and prosperity of the nation. As one of his first pupils, and after a life-long friendship, I may be permitted to testify that his energy in this cause was prompted by sincere convictions and not by political exigencies. Had Playfair lived a few months longer, we should never have had the misfortune to make the acquaintance of that new variety of *Homo sapiens* the 'conscientious objector,' who is just now giving so much trouble to our magistrates. This is not a time to sketch, even in merest outline, the epoch-making work of the Society, but I may at least state my conviction that it will be found, on comparing the volumes of our *Transactions* with those of the corresponding societies of other lands, that, considering the number of workers in each case, England is not behind any other nation in research work, and this in spite of the almost total absence of that lavish state aid which nearly every other civilised nation enjoys. In view of the vast number of discoveries pouring out from chemical laboratories,

I hear it suggested that the day is not far distant when there will be nothing left to discover, when all the elements in the cosmos shall have been captured and fitted into the Periodic System of Newlands and Mendeleeff, when there is not one more gas in the atmosphere left to be detected, and every element and group of elements shall have its ortho-, para-, and meta-position assigned to it. What will then remain to be done? Fortunately for investigators, we shall still be only as children gathering pebbles on the shore of the great ocean of knowledge. As yet we have only found the big boulders. To change the metaphor, chemistry now occupies the position of geography a century ago. The enormous number of chemical compounds are like so many islands, their latitude and longitude ascertained with precision, but on which the foot of man has not been put down, whilst their animals, plants, and minerals have never been exploited. When the ideal state of knowledge has been attained, chemists will perhaps find time to explore this vast archipelago, in which, there is no doubt, many interesting discoveries await those who shall undertake the task. Who can set a limit to the usefulness of these explorations? Even the most unpromising compounds may turn out valuable prizes! When aniline, chloroform, and carbolic acid were discovered, who could have predicted the revolutions in the arts and surgery which these bodies were destined to produce! They were but as desert islands until they attracted the attention of Hofmann, Perkin, James Simpson, and Lister. As chemists, I believe we have a noble future before us. Chemistry is distinguished from all other branches of knowledge as the helpmate of nearly every other science. The geologist, the botanist, and the physiologist find no thoroughfare unless they call in the help of the chemist. As soon as the physicist breaks into a molecule, he is trespassing on our domain. The bacteriologist has found that it is not the waggling of the tail of a pathogenic microbe that is the most important feature of its history, but that the chemical compounds which it secretes demand his closest attention. Even the astronomer has already to sit at the feet of the chemist! Thirty-three years ago, when our worthy President was but a youth, there was once a dinner party composed chiefly of chemists held at the Albion. A few are still living—among them being Sir F. Abel, Prof. Odling, and myself. In an after-dinner speech on that occasion, my friend Abel is reported to have expressed himself in blank verse as follows:—(I hope he will forgive me, at this distance of time, for appropriating his words to my own use).

"'Looking to right and to left, I see many faces around me,
Faces so old and familiar I feel once again at the College,
Testing, as in former times, for chlorine with nitrate of silver;
Gazing with youthful delight at crystals just hatched in a beaker,
Yearning o'er aniline drops distilling from crystal alembic.
O! my dear friends, one and all, we have toiled up a difficult pathway!
Some are low down on the hill, and others are near to the summit.
Let us remember the past and forget not our absent companions;
Fortune may come to us all; but youth will return to us never!'"

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, November 25th, 1898.

Mr. SHELFORD BIDWELL, F.R.S., President, in the Chair.

MR. R. A. LEHFELDT read a paper on "*The Properties of Liquid Mixtures*," being Part III. of his communications on that subject.

It deals with partiably Miscible Liquids. Measurements are given of the vapour-pressure of mixtures of phenol and water. This pair of liquids is completely miscible above 68° C., and incompletely miscible below that temperature. The law of equilibrium between incomplete mixtures and the vapours over them is investigated, especially at "the critical point," *i.e.*, at the point where incomplete miscibility passes over into complete miscibility. It is pointed out that normal organic liquids always mix completely. Ethylene dibromide and formic acid mix on boiling, and separate into two layers when cold. The curves representing the cases of complete mixture are comparable in shape with those previously obtained by Mr. Lehfeldt for mixtures of alcohol and toluene, but they show a still flatter maximum; so much so that 60 per cent to 70 per cent of phenol may be added to water without apprecible effect on the vapour-pressure. To verify this point a differential pressure-gauge was designed; the construction and method of using are given in the paper. The behaviour of the liquid is apparently the same above and below the critical point. At temperatures not too close to the critical point the vapour-pressure of a saturated mixture is approximately the sum of the partial pressures, calculated for the two saturated solutions according to Raoult's law. Diagrams are drawn showing the characteristic surface for phenol-water mixtures, with the freezing points of water and of phenol traced out. Phenol melts under water at 1·5° C., and forms a cryohydrate containing 4·83 per cent phenol, melting at −1·0° C.

Prof. S. YOUNG (Abstract of Communication).—The statement of Mr. Lehfeldt that normal organic liquids always mix completely, should be qualified. There are pairs of normal organic liquids which, though miscible in all proportions, approximate closely to partially miscible liquids: *e.g.*, benzene (b. p. 80° C.) and normal hexane (b. p. 69° C.). When American petroleum is fractionally distilled, the benzene which is present in small quantity does not come over at about 80°, but mostly at about 65°; the most probable explanation appears to be that benzene and hexane behave, as regards distillation, like miscible liquids, a view which is confirmed by an investigation of the boiling-points, and also of the specific gravities of mixtures of the two hydrocarbons, an account of which has lately been read before the Chemical Society, by Messrs. Young and Jackson, The boiling-point curve is similar in general form to that of phenol and water, as shown by Mr. Lehfeldt, though the deviation from the ordinary form is not so marked. Ten per cent of benzine has practically no influence on the boiling-point of normal hexane, but 10 per cent of hexane lowers the boiling-point of benzine nearly 3° C. Also there is always expansion on mixing benzine and hexane, the maximum reaching about 0·4 per cent.

Dr. S. P. THOMPSON asked whether any relation had been observed between the vapour-pressure and the surface tension of the mixtures.

Mr. LEHFELDT was not sure whether the surface-tensions of the components pass into one another at the critical point of mixture.

Mr. L. N. G. FILON then gave an account of his paper on "*Certain Diffraction Fringes as Applied to Micrometric Observations.*"

It is to a great extent a critical investigation of a paper by A. A. Michelson on the same subject (*Phil. Mag.*, vol. xxx., pp. 1—21, July, 1890).

Michelson there describes a method for measuring the angular distance between the components of a double star, or the angular dimensions of very small celestial bodies, by means of interference-fringes, using two adjustable slits in front of the objective of a telescope. If the star is double, or if it has an appreciable disc, then by widening the distance between the slits, the fringes become fainter, and in some cases almost vanish. But by still further widening the slit, the fringes reappear, disappear, and so on. In the paper (*l.c.*) Michelson develops the law of these appearances and disappearances, and gives an expression for the ratio of the angular distance between

the components of the double star, or the angular radius of the single source, to the distance between the slits, *on the assumption that the slits are infinitely long and infinitely thin.* Mr. Filon considers that this assumption is unjustified by the conditions of measurement; he reviews the original investigation, and modifies the results. He then proceeds to find equations to represent the intensity of light in the focal plane, for a point-source, and for a two-point source. These fringes are only visible over a certain rectangle, called "the rectangle of illumination" of the source. In the case of a two-point source, if the distance, perpendicular to the slits, between the geometrical images of the two points, is an integer-multiple of the distance between two fringes, the maxima of one system correspond with the maxima of the other, the fringes overlap, and their intensity is augmented. If, however, this distance should be an odd multiple of the half distance between the fringes, the maxima of one system correspond to the minima of the other, and if *the fringes that are superposed* are of similar intensity, the fringing is nearly obliterated, a result that agrees with Michelson's law. But it is now shown that for this phenomenon to occur (1) the rectangles of illumination of the two sources must overlap to a very large extent—this consideration was neglected by Michelson; and (2) the angular distance between the two stars, measured parallel and perpendicularly to the slits, must be less than a definite amount, depending upon the wave-length and the length and breadth of the slits. In astronomical cases, the second condition is generally satisfied. If the rectangles of illumination do not overlap they can be respectively distinguished, and thus the star can be resolved by direct observation. If, however, an accurate measurement of the distance between the components is required by Michelson's method, the rectangles must be made to overlap. The paper includes an investigation of a refractometer that Michelson (*l. c.*) proposed to use for increasing the effective aperture of a telescope; it is shown that Michelson's law is generally true for that instrument, but certain limitations are pointed out. Extended sources are next considered, and also the shape and size of the object. The paper concludes with the description of a method by means of which the ellipticity of a very small disc may be measured by these diffraction fringes in the special case where Michelson's law holds good.

In reply to a question from Professor S. P. Thompson, Mr. Filon said that the minimum breadth of slit with which he had found it practicable to work, using monochromatic light with his telescope, was about half a millimetre.

The President proposed votes of thanks, and the meeting adjourned until December 9th.

NOTICES OF BOOKS.

Chemistry for Schools. An Introduction to the Practical Study of Chemistry. By C. Haughton Gill, late Assistant Examiner in Chemistry at the University of London, and Teacher of Chemistry and Experimental Physics in University College School. Tenth Edition. Revised and Enlarged by D. Hamilton Jackson, Ph.D. (Heid.), Demonstrator of Chemistry, Univ. Coll., Bristol. London: Edward Stanford, 26 and 27, Cockspur Street, Charing Cross, S.W.

For a book of comparatively so small a size, a considerable amount of information has been introduced. That it has reached a tenth edition shows that it is appreciated, and this edition has been brought up to the present date of knowledge. There are plenty of illustrations, and each chapter concludes with a series of questions bearing upon the subject under discussion. Whenever possible, pains have been taken to impress a statement by detailing a simple experiment that the student can perform himself: this is not only of great value as a means of fixing a truth firmly in the mind, but carries with it the charm of experiment—a matter of considerable moment in connection with elementary schools. No doubt there are many cases where a few simple experiments successfully carried out have decided the course of a boy's life.

A list of apparatus and chemicals, with prices and dealers' addresses, is given at the end of the book: this will be of use to those living in the country.

Metrical Tables. By Sir Guilford L. Molesworth. Third Edition, Revised and Enlarged. London: E. and F. N. Spon, Ltd., 125, Strand. New York: Spon and Chamberlain, 12, Cortlandt Street.

The value of Molesworth's Pocket-book Tables is so well known that little need be said beyond announcing the publication of this third edition. Now that the metric system has become so extended, a handy pocket-book containing a collection of useful tables has become almost indispensable.

There is a good index, and, as it is bound in limp cloth and is only a quarter of an inch thick, it can be easily carried in the pocket.

The Organised Science Series. First Stage: Inorganic Chemistry (Practical). For the Elementary Examination of the Science and Art Department. By Frederick Beddow, D.Sc., Ph.D. London: W. B. Clive, University Correspondence College Press, 13, Bookseller's Row, Strand, W.C.

Although professedly an examination book, the author has endeavoured to present his instruction in a sound, practical, and systematic way. Chapter I., Introductory Experiments, commences rather abruptly, "How to Bore a Cork," and simple descriptions are given of such useful operations as cutting and bending glass tubes, mounting platinum wires for flame tests, making a wash-bottle, &c. Then follows a list of the characteristic properties of some common substances, leading up to some simple quantitative experiments, and a note on weighing and the use of a balance; finally, a chapter is devoted to systematic analysis.

Although the matter is necessarily rather condensed, and the style somewhat abrupt, it is evident that the author has his object, "practical instruction," well in hand, and to an intelligent student the book will prove of real value.

CORRESPONDENCE.

ETHERION.

To the Editor of the Chemical News.

Sir,—The above so-called new constituent of the atmosphere discovered by Professor Brush was the subject of an article in the Chemical News of November 4th (vol. lxxviii., p. 221) by Sir William Crookes, who pointed out the probability of it being simply a residue of water vapour, but suggested that when the complete paper came to hand more light might be thrown upon the subject.

The American periodical *Science* for October 14th contains a complete account of the investigation, and on examination it fully bears out Sir William Crookes's forecast. The paper is very lengthy, but the one solitary fact put forward is that powdered glass, sand, charcoal, &c., on heating give up a gas which, at greatly reduced pressures (between fifty-millionths of an atmosphere and zero, as indicated by a special form of gauge), *in the*

absence of a drying agent, conducts heat better than hydrogen! Now this, as was pointed out, is precisely what one would expect to get if water vapour is present, and it seems to be meagre evidence upon which to base the tremendous assumptions which follow in the paper. It is conjectured that "etherion will be found to consist of three or more gases forming one or more periodic groups of new elements"; that "etherion will at least account for some of the phenomena at present attributed to the ether"; that "it may be the medium of propagation of Röntgen rays in the vacuum glass and air!"

The reasoning, too, in the paper strikes one as very strange, as in the following instances:—"A specimen of very fine white siliceous sand heated in vacuum . . . gave a considerable amount of the new gas." Glass that had been deprived of etherion was exposed in a thin layer to air and then found, on exhausting and heating, to yield it "as freely as at first." And another experiment is given in which "several days of high heating, with frequent exhaustion, failed to wholly deprive the pulverised glass of its new gas." "From this and other reasons" Professor Brush believes "the new gas resides *in*, and not simply on the surface of, glass!"

As an instance of the speculative part of the paper, the following extracts are amusing:—

A curve, *g h*, is given in the diagram (CHEMICAL NEWS, vol. lxxviii., p. 197) showing the conductivity of the gaseous residue between pressures of 43 millionths and 0·38 millionth of an atmosphere, and at this last pressure the conductivity was found to be twenty-seven times that of hydrogen under the same conditions. Another curve, *o p*, gave at $p = 0{\cdot}12$ millionth, a conductivity forty-two times that of hydrogen, and it is concluded as "reasonably certain" that, if the curve *e f* had been carried to as low a pressure as *o p* it would have shown a conductivity of at *least one hundred times that of hydrogen*. On this astonishing assumption, the following table of molecular weight, density, specific heat, &c., is constructed:—

Comparison of Gaseous Properties.

1. Gas.	2. Molecular wt.	3. Density, D.	4. Relative specific heat.	5. Relative molecular velocity, $\frac{1}{\sqrt{D}}$	6. Relative heat conductivity.
Etherion	?0·0002	?0·0001	6000·?	100·?	100·
Hydrogen	2·	1·	1·	1·	1·
Helium	4·	2·	?0·300	0·71	0·73
Carbon monoxide	27·8	13·9	0·072	0·27	0·33
Air	28·8	14·4	0·069	0·26	0·32
Carbon dioxide..	43·8	21·9	0·064	0·21	0·21

Later on in the paper it is pointed out that the values given are only intended to indicate the order of magnitudes expected to be found on further investigation; but one cannot help thinking that, until very much further investigation has been made, there will be no need either to modify our views of the ether, the Periodic Law, or even to burden ourselves with a still further host of "new constituents of the atmosphere."—I am, &c.,

PHYSICIST.

THE GASES OF THE ATMOSPHERE.

To the Editor of the Chemical News.

SIR,—Your readers will, I suppose, hardly expect Professor Ramsay to reply to the letter of your correspondent, "Suum Cuique," who has again addressed you on the question of the respective shares of Lord Rayleigh and Professor Ramsay in the discovery and subsequent isolation and study of argon. This is a subject of which I believe most chemists will feel that we have heard enough, more especially as Lord Rayleigh has himself expressed in the clearest possible terms his own feeling in regard to Professor Ramsay's share in the investigation. On the occasion of the annual meeting of the Chemical Society in March, 1895, after receiving the Faraday Medal from the hands of the President, Lord Rayleigh is reported to have spoken as follows:—

"He said that in returning his thanks to the Society, he was somewhat embarrassed because he felt that there ought to be another standing at his side. It was true that his researches, to which the President had referred, upon the densities of gases had rendered it almost certain that a new gas of some sort was concerned and probable that the new gas was in the atmosphere. But from this point to the isolation and examination of argon was a long step, and the credit for it must be shared equally between Professor Ramsay and himself. In some quarters there had been a tendency to represent that antagonism existed between chemists and physicists in the matter, though such a thought never entered his mind. Professor Ramsay was a chemist by profession, while he himself had dabbled in chemistry from an early age, and had followed its development with a keen interest." (See *Trans. Chem. Soc.*, 1895, p. 1107).

In the same year the Davy Medal was awarded to Professor Ramsay by the Council of the Royal Society, of which Lord Rayleigh was then a member and an officer. In conformity with an unwritten but very salutary rule, officers of the Society are debarred from receiving medals or other awards under the control of the Council during their tenure of office. Lord Rayleigh had, however, been the recipient of the highest honour which the Chemical Society has it in its power to bestow, and it is fair to surmise that he concurred in the award of the Davy Medal to his coadjutor in this work. If Lord Rayleigh had been dissatisfied his colleagues on the Council were in a position to be aware of it, but no hint of such a feeling has ever escaped him, and the award was felt by everybody outside to be just.

Is "Suum Cuique" so much in the confidence of Lord Rayleigh that he can pretend to know what conversations occurred between him and the numerous chemists whom he consulted, or that he is in a position to say that the Cavendish experiment was not mentioned by more than one of them?

Professor Ramsay says that he directed Lord Rayleigh's attention to the Cavendish experiment, and because he says so I believe him, and shall continue to do so until, or unless, Lord Rayleigh states the contrary. This up to the present he has not done.

The writer of anonymous letters may escape the charge of vanity, but when his communications assume the character of those which bear the signature of "Suum Cuique" they are open to the more serious charge of malice.

This unknown champion will scarcely ask us to believe that he is authorised by Lord Rayleigh to defend his scientific character. Lord Rayleigh's name is honoured throughout the civilised world; his reputation does not require to be propped up by anonymous support, neither does it hang upon such slender threads as suggested in the successive letters of your correspondent.—I am, Sir, &c.,

WILLIAM A. TILDEN.

Royal College of Science, London,
Nov. 28th, 1898.

The Sugar in Orange-peel.—J. Flatau and H. Labbé.—While trying to isolate in a state of purity the odorous ether which exists in essence of orange, the authors noticed that it was always accompanied by a very small quantity of a substance easily soluble in water, and after treating a quantity of the peel in a certain manner they succeeded in isolating a substance presenting all the characteristics of a sugar. To identify this sugar they prepared its hydrazone by Emile Fischer's method, and finally decided that it was mannose.—*Bull. Soc. Chim. de Paris.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 5, August 1, 1898.

Action of Pure Phosphoretted Hydrogen on Copper Sulphate.—E. Rubénvitch.—Previous investigators obtained a black precipitate by the action of phosphoretted hydrogen on copper sulphate, of an indefinite composition. The author investigates the subject thoroughly. He acts on a measured quantity of copper sulphate with phosphoretted hydrogen, then filters the precipitate, and washes with distilled water freed from air. All these operations take place in a vacuum. The copper phosphide is well defined and free from metallic copper; it corresponds to the formula $P_2Cu_5.H_2O$. Apparently the reaction takes place in two stages; two unstable phosphides being first formed, which, in the presence of the oxygen of the air, are transformed—one into metallic copper and phosphoric acid, and the other into a black compound containing oxygen. In the absence of all traces of oxygen, the reaction takes place according to the equation—

$$10CuSO_4+5PH_3+6H_2O= \\ =2P_2Cu_5.H_2O+PO_4.H_3+10H_2SO_4.$$

Copper phosphide dissolves in strong sulphuric acid with evolution of phosphoretted hydrogen. Nitric acid and bromine attack it easily, and it reduces permanganate of potash.

Action of Bromine on Normal Propyl Bromide in presence of Anhydrous Aluminium Bromide.—A. Mouneyrat. — The production of hexabromethane (CBr_3—CBr_3) by bromination with anhydrous $AlBr_3$ of ethyl bromide in successive stages has already been discussed. The present paper treats of the application of the same method to propyl bromide. Derivatives of propane were obtained with have hitherto been satisfactorily produced by no direct method. A solution of aluminium bromide in bromine was used; the given substance and the bromine being in theoretical proportions, corresponding to the general equation—

$$C_3H_xBr_y+Br_2=C_3H_{(x-1)}Br_{(y+1)}+HBr.$$

No. 6, August 8, 1898.

Hydrolysis of Ethane Dipyrocatechin.—M. Moureu.—In a previous publication, the hydrolysis of ethane dipyrocatechin by means of boiling dilute sulphuric acid has been discussed. The products are pyrocatechin and the substance $C_8H_8O_4$. Thus:—

$$C_6H_4\!<\!\begin{matrix}O\\O\end{matrix}\!>\!CH-CH\!<\!\begin{matrix}O\\O\end{matrix}\!>\!C_6H_4+2H_2O= \\ =C_6H_4\!<\!\begin{matrix}OH\\OH\end{matrix}+C_8H_8O_4.$$

By means of various reactions, the author has found the constitution of the substance $C_8H_8O_4$ to be represented by the formula $C_6H_4\!<\!\begin{matrix}OH\\O-CH_2-COOH\end{matrix}$, viz., orthoxyphenyloxyacetic acid; this has been confirmed by synthesis. This body loses water when distilled, giving the anhydride, $C_8H_6O_3$, or $C_6H_4\!<\!\begin{matrix}(1)O-CO\\ \quad\quad|\\(2)O-CH_2\end{matrix}$. The latter substance, which is the aldehyd glyoxalmonopyrocatechin, $C_6H_4\!<\!\begin{matrix}(1)O\\(2)O\end{matrix}\!>\!CH-CHO$, apparently constitutes the first intermediate product of the hydrolysis of ethane-dipyrocatechin, furnishing, by further hydrolysis, orthoxyphenyl-oxyacetic acid. That this surmise is correct is demonstrated by the hydrolysis of the compound $C_6H_4\!<\!\begin{matrix}(1)O\\(2)O\end{matrix}\!>\!CH-CH\!<\!\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$, which is simply the diethyl acetal corresponding to the above-mentioned aldehyd. The hydrolysis of this acetal was effected by Julius Hesse (*Comptes Rendus*, cxxvii., p. 276), and the product resembled in all respects the orthoxy-phenyl-oxyacetic acid of the author.

No. 7, August 15, 1898.

Atmospheric Carbonic Acid.—Albert Lévy and H. Henriet.—To collect the carbonic acid in the atmospheric air, the latter is allowed to bubble rapidly through a dilute solution of potash or baryta. The authors have investigated the amount present during the day, night, and at different times of year. They found—(1) that by their method all the free CO_2 was retained by the potash (this being proved by connecting a second potash tube on to the first, which did not vary in weight); (2) there was always less than half a litre of CO_2 to 100 m.c. of air; (3) that dilute solutions of various alkalis give exactly the same results; (4) that the variation in the amount of CO_2 in the air was very small during six years. If a globe of air which had been freed from CO_2 was left for some time in contact with potash, fresh CO_2 was formed. This showed that in the air there were carbonaceous substances, which in presence of oxygen and an alkali form CO_2. The amount of CO_2 formed was considerably more after the air had been left in contact with alkali for two hours than after ten minutes; but after two hours no increase in the amount was perceived, showing that the whole of the carbon was probably transformed into CO_2 in about two hours. The author gives tables of results for every day during three or four weeks.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xxxi., March 14, 1898.

Formation of Metallic Sodium by means of Peroxide of Sodium.—H. Bamberger.—It is very easy to prepare metallic sodium as a lecture experiment by means of the peroxide. To effect this it suffices to heat the latter with charcoal, graphite, or coke in a covered crucible to about 300—400°. The reaction is rather violent and should only be performed on a few grms. at a time; most of the sodium is deposited on the cover and the sides of the crucible, $3Na_2O_2+2C=2Na_2CO_3+Na_2$. Peroxide of sodium reacts still more violently with carbide of calcium. If an excess of carbide be used, amorphous carbon is deposited, and a part of the carbide remains undecomposed. When the residue is decomposed by water, in the first case hydrogen is given off, and in the second case hydrogen and acetylene.

Action of Acetic Anhydride on the Anilides of the Bibasic Acids.—H. de Pechmann and W. Schmitz.—Oxanilide boiled for a long time with acetic anhydride and acetate of sodium reacts according to the equation—

$$\begin{matrix}CO.NH.C_6H_5\\|\\CO.NH.C_6H_5\end{matrix}+COOH.CH_3= \\ =\begin{matrix}CO.N(C_6H_5)\\|\\CO.N(C_6H_5)\end{matrix}\!>\!C=CH_2+2H_2O.$$

A vinylidene-oxanilide is formed, enclosing a pentagonal nucleus with two atoms of nitrogen.

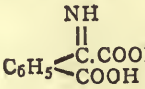
Action of Aniline on Dioxytartaric Acid.—A. Reissert.—The author has endeavoured to prepare the unknown dianilsuccinic acid by the action of aniline on dioxytartaric acid, $\begin{matrix}C_6H_5-N=C-CO_2H\\|\\C_6H_5-N=C-CO_2H\end{matrix}$. This body,

or, at any rate, the monoanilidoxysuccinic acid, $C_6H_5N=C(CO_2H)-(OH)_2=C(CO_2H)$, seems to be the first product formed in the reaction, but it decomposes so rapidly that it cannot be isolated. When dioxytartaric acid is added to hydrochlorate of aniline, CO_2 is given off, and, according to the proportion of the base present, we obtain salts of aniline, anilidomalonic acid, or anilidomalonanilic acid. Anilidomalonic acid, $C_9H_9NO_4$, crystallises in white needles fusible at 121°, easily soluble in warm water and alcohol, less soluble in ether, and difficultly so in benzene and ligroïn. The free acid and the ammonia salt take an intense brownish red colour with Fe_2Cl_6. Anilidomalonanilic acid, $C_{15}H_{14}N_2O_3$, takes the form of microscopic needles fusible at 157°, decomposing into aniline and CO_2. It is soluble in the alkalis and the alkaline carbonates, insoluble in water and the organic solvents, it gives a yellow colour with Fe_2Cl_6, and is easily transformed into the preceding acid.

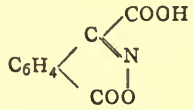
Dinitrodibenzoyldisulphonic Acid. (II.).—C. Ris and C. Simon.—The authors add several details on the method of preparing pure dinitrodibenzoyldisulphonic acid, and confirm the observations of Green and Wahl, according to whom the sodium salt of this acid, when pure, does not give a coloration with soda-lye and phenylhydrazin. When this salt of sodium is treated with hydrochloric acid, we obtain an acid salt and not a free acid. The analysis of the neutral sodium salt gives a result which does not correspond with its supposed constitution, but to a compound containing one atom of oxygen less. The percentage composition is that of a nitroso-nitrated derivative, but its constitution has yet to be determined.

Sulphonals of Cyclic Ketones.—O. Wallach and W. Borsche.—The authors, taking into consideration the tendency of the cyclic ketones—in the same manner as acetone—to give products of condensation, have prepared the sulphonates of several cyclic ketones. Into a mixture of one molecule of pentanone and two molecules of ethylmercaptan, kept at the temperature of melting ice, they passed dry hydrochloric acid gas until saturation, and then oxidised the product formed; they obtained the sulphonal of pentanone, $CH_2(CH_2)_3CH_2>C(SO_2C_2H_5)_2$, insoluble in water, crystallising in alcohol and fusing at 127—128°. In the same manner, the sulphonal of methylpentanone, crystallising in prisms and melting at 110·5—111·5° was obtained; also the sulphonal of methylhexanone, difficultly soluble in cold water, melting at 104—105°; and the sulphonal of heptanone crystallising in absolute alcohol in prisms, and melting at 136—138°.

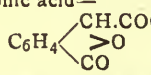
Phthalonic Acid.—C. Graebe and F. Trümpy.—Phthalonic acid forms an excellent substance to use for the preparation of a series of derivatives such as phthalaldehydic acid, phthalide, homophthalic, hydrodiphthallactonic, and β-desoxybenzoïn-carbonic acids. Phthalonic acid crystallises with 2 aq, which it loses slowly at 80—100°, and more rapidly at 110—120°; the anhydrous acid melts at 144·5°. When heated it forms, not only phthalic acid, but also phthalaldehydic acid, which becomes transformed into its anhydride and biphthalyle. Phthalonic acid evaporated on the water-bath with an excess of ammonia gives an acid with the probable constitution—



this acid, slightly soluble in water, dissolves easily in alcohol, giving an intense yellow colour. Hydroxylamine gives, with phthalonic acid, an oxime,—

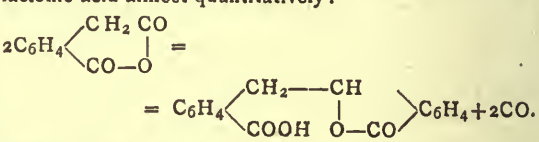


or a phthalimide according to the conditions. Treated with sodium amalgam, phthalonic acid becomes changed into phthalidcarbonic acid—



This can also be obtained by reduction in an acid solution by means of zinc powder or magnesium.

Homophthalic Acid.—C. Graebe and F. Trümpy.—The authors have prepared homophthalic acid by heating 10 grms. of phthalonic acid with 2 grms. of red phosphorus and 12 c.c. of HI of density 1·67 and 3 c.c. of water, for three or four hours, with a vertical condenser attached. When heated to about 190° this body becomes anhydrous; when further heated to 210—230° it forms hydrodiphthallactonic acid almost quantitatively:—



They have also prepared β-desoxybenzoïn-carbonic acid, which changes into isobenzal phthalide when heated to 200°.

Action of Diethyloxalic Ether on *p*-Amidophenol and its Ether.—A. Piutti and R. Piccoli.—A controversial paper not suitable for abstraction.

The Derivatives of Benzalacetophenone containing Nitrogen.—J, Tambor and F. Wildi.—The authors find that benzalacetophenone reacts with ammonia and the primary aromatic amines, while up to the present time the secondary aromatic bases, pure and mixed, have resisted this reaction, which is generally carried out in the cold, and as a rule with the absence of alkali. The products of condensation are generally white, but if, however, they contain a chromophore group, such as NO_2 for example, they become yellow or red. The authors have prepared dibenzalacetophenoneamine by condensing the benzalacetophenone with ammonia in alcoholic solution, and dibenzalacetophenone-nitrotoluidine, as well as the corresponding derivatives of the three isomerous nitranilines and of α-naphthylamine.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Society of Arts, 8, (Cantor Lectures). "Acetylene," by Prof. Vivian B. Lewes.
—— Society of Chemical Industry, 8. "On Oxone and its Commercial Applications," by Colonel W. J. Engledue, R.E. "An Improved Apparatus for the Estimation of Carbonic Acid in Minerals, &c.," and "The Preparation of Standard Solutions of Sulphuric Acid," by Arthur Marshall.
—— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 6th.—"The Yangtse Basin and the British Empire," by Archibald Little, F.R.G.S.
WEDNESDAY, 7th.—Society of Arts, 8. "Egypt and the Soudan in 1897 and 1898," by W. T. Maud.
FRIDAY, 9th.—Physical, 5. "Longitudinal Vibrations in Solid Hollow Cylinders," By C. Chree, Sc.D., F.R.S., &c. "Thermal Properties of Normal Pentane," by J. Rose-Innes, M.A., B.Sc., and Sydney Young, D.Sc., F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2037.

ON THE CONDENSATION NUCLEI PRODUCED IN GASES BY THE ACTION OF RÖNTGEN RAYS, URANIUM RAYS, ULTRA-VIOLET LIGHT, AND OTHER AGENTS.*

By C. T. R. WILSON, M.A.,
Clerk-Maxwell Student in the University of Cambridge.

The experiments here described consist mainly in determinations of the least degree of supersaturation necessary to cause water vapour to condense on nuclei from various sources.

As in former experiments (*Phil. Trans.*, A., 1897, vol. clxxxix., p. 265; *Camb. Phil. Soc. Proc.*, 1897, vol. ix., p. 333) the supersaturation is brought about by very sudden expansion of air or other gas originally saturated with water vapour, the expansion required to produce a fog or shower of drops being measured. The expansion is expressed in terms of v_2/v_1, the ratio of the final to the initial volume.

The following classes of nuclei have been studied in this way:—

1. Nuclei produced by Röntgen rays.
2. ,, ,, uranium rays.
3. ,, ,, ultra-violet light.
4. ,, ,, sunlight.
5. ,, ,, metals in contact with the gas.
6. ,, ,, the action of ultra-violet light on a negatively electrified zinc plate.
7. ,, ,, the discharge of electricity from a pointed platinum wire.

In addition the behaviour of the nuclei in an electric field has been studied, with the object of distinguishing between "ions" and nuclei which carry no charge of electricity.

1. The action of strong X rays on the gas differs from that of weak rays (*Phil. Trans., loc. cit.*) merely in the number of nuclei produced, the supersaturation required to cause water to condense on the nuclei remaining unaltered. The value of v_2/v_1 corresponding to this degree of supersaturation (approximately fourfold) is equal to 1·25.

2. Uranium compounds, whether inside the expansion apparatus in immediate contact with the gas or contained in a glass bulb outside the apparatus (*Camb. Phil. Soc. Proc., loc. cit.*), produce nuclei requiring the same degree of supersaturation as those produced by X rays.

(Expansion experiments probably furnish one of the most delicate methods of detecting these rays).

3. Ultra-violet light acting on moist air or oxygen produces nuclei which, when the radiation is weak, require quite as great a degree of supersaturation to cause water to condense on them as those produced by X rays. With stronger radiation, however, the nuclei appear to grow, the expansion required to produce a cloud now depending on the strength of the radiation and on the time for which the gas has been exposed to the rays before expansion. With very strong ultra-violet light the growth of the nuclei, even in unsaturated air, continues till they become visible, as stated in a preliminary note (*Camb. Phil. Soc. Proc.*, 1898, vol. ix., p. 392). The phenomena are then like those observed by Tyndall with certain vapours exposed to ordinary light. That nuclei are produced when ultra-violet light enters an expansion apparatus through a quartz window was discovered by Lenard and Wolff, but they believed them to arise from disintegration of the quartz. That these nuclei arise not at the quartz, but throughout the volume of the air exposed to the rays, is capable of experimental proof in a variety of ways. In hydrogen even strong ultra-violet light produces comparatively few nuclei, these requiring also as great a degree of supersaturation as the nuclei produced by X rays in order that water may condense on them.

4. Sunlight produces in air nuclei which require large expansions (v_2/v_1 about 1·25) in order that water may condense on them.

5. Certain metals in moist air produce nuclei, always requiring great supersaturation in order that condensation may take place on them. The supersaturation required is generally as great or greater than that required in the case of X ray nuclei. In the presence of amalgamated zinc dense fogs are obtained with expansions, which in the absence of the metal only result in the formation of a very few drops. Clean surfaces of zinc or lead have a similar but much slighter effect; with copper or tin it is inappreciable. These phenomena are obviously closely connected with the effects which these metals exert on a photographic plate, studied by Russell and others.

6. Ultra-violet light acting on a negatively electrified zinc plate produces condensation nuclei, as was proved by the steam jet experiments of Lenard and Wolff. The nuclei, however, are not, as these observers supposed, produced by disintegration of the metal, for expansion experiments show that they are identical with the nuclei produced by X rays with respect to the degree of supersaturation required to cause condensation to take place on them, and therefore entirely unlike dust particles. In hydrogen the maximum number of drops in the fogs which result on expansion is obtained with comparatively weak fields; no nuclei are produced when the zinc is positively electrified.

7. The discharge from a pointed platinum wire in moist air or hydrogen produces nuclei which also require approximately the same expansion, $v_2/v_1 = 1{\cdot}25$, in order that condensation may take place on them. If the expansion be made while the discharge is taking place no fog is obtained with smaller expansions. The results are not so simple if the expansion be made after the discharge has ceased, apparently on account of some secondary effect of the discharge causing the nuclei to grow. No nuclei were produced unless a glow could be observed at the point of the wire.

Effect of an Electric Field.—When air exposed to X rays is enclosed by two parallel plates, between which a sufficient difference of potential is maintained, the fogs obtained on expansion are very much less dense than in the absence of the electric field, and if the rays be turned off before expansion all the nuclei are found to have been removed, whereas without any electric field a fog is obtained even if the expansion be not made till some seconds after the rays have been cut off. This behaviour of the nuclei proves them to be charged particles or "ions." The nuclei produced by uranium rays behave in a similar manner; those produced by the action of ultra-violet light on moist air, or by the presence of metals, are entirely unaffected by an electric field. They are therefore not ions but uncharged nuclei. (Since the nuclei produced by the action of metals on air or by weak ultra-violet light require just as great a degree of supersaturation as those produced by X rays to cause water to condense on them, the difference in the behaviour of the two classes of nuclei can scarcely be due to a difference in size). The nuclei which escape from a negatively electrified plate under the influence of ultra-violet light are of course charged.

It follows from the experimental results described in this paper that the passage of electricity through gases is effected by charged particles which have an identical effect as condensation nuclei, whether the conduction is the re-

* Abstract of a Paper read before the Royal Society, November 24, 1898.

sult of exposure of the gas to X rays or uranium rays, or of the action of ultra-violet light on a negatively charged zinc plate, or consists in the escape of electricity from a pointed platinum wire. In all cases the degree of supersaturation required to make condensation take place on these particles is approximately fourfold (*Phil. Trans., loc. cit.*).

The nuclei which are produced and grow (in air or oxygen under the action of ultra-violet light are uncharged, in their initial stages at least; they are therefore not electrified water drops. It is possible that they are water drops containing in solution some substance, perhaps H_2O_2, produced within them by the action of the ultra-violet light in quantities sufficient to counterbalance the effect of the curvature of the surface upon the vapour pressure necessary for equilibrium.

EXAMINATION AND SEPARATION OF THE EARTHS OF MAGNESIA, AND OF OXIDE OF MANGANESE, IN THE PRESENCE OF ACIDS FORMING INSOLUBLE SALTS WITH THESE BODIES.

By M. A. VILLIERS.

In the qualitative examination of bases the precipitate obtained by adding an excess of ammonia to the solution resulting from a previous treatment by sulphuretted hydrogen after peroxidation of the iron, and in presence of hydrochlorate of ammonia, may, as is well known, have a more or less complex composition. In the absence of acids which form insoluble salts with these bases, such as lime, it cannot contain any other metals besides iron, chromium, and aluminium. In the contrary case it may contain a part or the whole of the lime, baryta, strontia, manganese, and magnesia.*

In all analytical treatises one is obliged to give two methods to be followed in the study of the ammoniated precipitate, according as we have to deal with one or other of these cases. Besides this inconvenience, the examination of the eight metals which may enter into the composition of this precipitate is always long and delicate. Further, we have to test for and separate the lime, baryta, strontia, manganese, and magnesia, twice,—in the ammoniacal precipitate and in the filtered liquid.

It is easy to avoid these inconveniences and to obtain —no matter what the original solution may be—a precipitate containing only the three sesquioxides.

Let us first see which are the acids whose presence may cause the precipitation by ammonia of other bases than the three sesquioxides.

We first eliminate silicic acid, which is easily separated by evaporation to dryness, after the addition of hydrochloric acid.

In the same manner the solution, after treatment with sulphuretted hydrogen, should be freed from carbonisable organic acids, such as tartaric and citric acids, whose presence would prevent the precipitation of the sesquioxides.

There is no need to try and separate boric acid. The borates are too soluble in the presence of ammoniacal salts to make it necessary to test for them in the washed precipitates.

There therefore remain oxalic acid and phosphoric acid. We shall show later on how easily the first can be destroyed and the second separated. It is in an acetic solution and in the state of ferric phosphate that we can effect this separation. This well-known method for the elimination of phosphoric acid does not appear up to the present to have given results of indisputable accuracy in the separation of this acid and the alkalies. It can, however, be adapted to the qualitative and quantitative separation of phosphoric acid, as well as of lime, baryta, strontia, manganese, and magnesia, and further this separation is as complete as in the case of the alkalies, if carried out under favourable conditions.

Although the earthy phosphates and phosphate of manganese are soluble in acetic acid, it is not sufficient that the acetic solution should contain a quantity of ferric salt theoretically sufficient for the precipitation of the phosphoric acid, or that it should be added. We have noticed, in fact, that even with solutions containing a notable excess of iron, the precipitate obtained by boiling after the decomposition of the acetate of iron, separated by filtration from the solution freed from phosphoric acid, after thorough washing, may contain a large proportion of the earthy metals and of manganese. This entanglement is probably due to the formation of double salts, insoluble in acetic acid.

In the same way if—to an acid liquor containing a ferric salt and a base such as lime in the presence of phosphoric acid—we add an excess of ammonia, the precipitate thus obtained treated with acetic acid will give up none, or only a part, of the lime it contains, and that even when the iron is in excess with regard to the phosphoric acid. And again, freshly formed phosphate of iron, added to a solution of the chloride of the earthy metals, retains a large proportion of these latter when the solution is made alkaline with ammonia.

Phosphoric acid cannot be completely separated in the state of ferric phosphate from the earths and from manganese in acetic solution, except when we have a very large excess of iron in proportion to the phosphoric acid present. We shall see below how to make quite certain that this excess is sufficient. We will now describe the method to be followed for the separation of the three sesquioxides from the following metals :—

Experiments on Fe, Cr, Al, Ca, Ba, Sr, Mg, Mn, in the presence of Acids forming Insoluble Salts with these Metals.

If necessary the organic matter is first destroyed by calcination. The silica is eliminated by evaporation to dryness in the presence of hydrochloric acid.

Phosphoric acid is tested for in a small portion of the solution by means of molybdate of ammonia.

Oxalic acid is also tested for :—

1. In the presence of phosphoric acid: if a test on a small portion indicates the presence of manganese, the presence of oxalic acid will be manifested by a disengagement of CO_2, making the solution cloudy with baryta, at the moment when the liquor resulting from the treatment with sulphuretted hydrogen, after acidulating with hydrochloric acid, is peroxidised with nitric acid. If no manganese is present we add a few drops of chloride or of nitrate of this metal to a portion of the solution, and make the same test.

2. In the absence of phosphoric acid we test for oxalic acid by means of a *salt of lime* and *acetate of soda*.

If oxalic acid is found to be present it must be destroyed in the whole of the solution, either by calcination (it cannot be present if we have already destroyed the carbonisable organic matters) or by the action of hydrochloric and nitric acids and of a salt of manganese, prolonged until CO_2 is no longer given off. If the solution does not contain a manganese salt, and it has to be added, account must be kept of the amount added in the subsequent results.

In the absence of phosphoric acid the testing for bases is conducted in the ordinary manner, and the sesquioxides are precipitated by ammonia.

If phosphoric acid is present it must be removed, after peroxidation of the iron, in the state of ferric phosphate,

* As for the zinc, cobalt, and nickel, it is quite a mistake to include them in certain analytical tables: they do not form permanent precipitates, insoluble in excess of ammonia, even in the presence of acids forming insoluble salts; always on one condition, and that is—that enough ammonia or ammonia salts has been added

at the same time as the three sesquioxides are separated. We partially neutralise by adding ammonia, drop by drop, until the precipitate commences to appear; re-dissolve the precipitate in the smallest possible quantity of hydrochloric adid, then add a *small quantity* of an *alkaline acetate*.

If the iron is in great excess this addition will not cause precipitation in the cold, on account of the solubility of ferric phosphate in the ferric salts. If, on the other hand, a precipitate is formed, we add a small quantity of *perchloride of iron* (iron has been found by a previous test), and we wait a few instants to see if the solution becomes limpid again. If necessary fresh quantities of perchloride of iron are added, to obtain complete solution, and this is verified by the addition of a drop of an alkaline acetate, which should not produce a precipitate; if it does, more acetate and perchloride of iron must be added.

It only now remains to dilute with water if the colour is very intense, and boil for some instants. If the solution remains coloured, acetate must be gradually added until the colour disappears. Filter while boiling. (If this operation takes much time, traces of iron may be re-dissolved, thanks to the carbonic acid in the air; this is removed by boiling the filtrate and passing it through a second filter.

The solution is re-heated with a slight excess of ammonia; if a further precipitate of sesquioxides is formed, it must be collected on another filter and added to the preceding one.

In the precipitate the sesquioxides are found; and in the solution concentrated by evaporation, the bases comprising the earths and the manganese, in the ordinary manner.

We may remark that the separation of the manganese from the sesquioxides, being made here in acid solution, is much more distinct than when these latter are precipitated by ammonia; for in the latter case it is almost impossible to prevent, during the filtration and washing, the action of the air on the liquid, with the precipitation of a small part of the saline oxide of manganese which will be thus found mixed with the precipitate.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 15.

NOTE ON

A TUNGSTO-POTASSIC TUNGSTATE, AND A NEW METHOD OF PREPARING BINOXIDE OF TUNGSTEN.

By L. A. HALLOPEAU.

By submitting acid tungstate of soda heated to redness to the action of hydrogen, Wöhler obtained cubical crystals possessing the colour and brilliancy of metallic gold; he considered this compound to be a bitungstite of sodium, $Na_2O.2WO_2$, but some years later Malaguti showed that this formula was incorrect, and that the compound in question was what he called a *tungstate of sodium and of tungsten*, with the formula $Na_2O.WO_3+WO_2.WO_3$.

Shortly afterwards Laurent prepared, by Wöhler's method, a body by the reduction of tungstate of potassium, which he obtained in small needles of a deep coppery violet-red colour, resembling sublimed indigo; but he gave no indication as to the probable composition of this body, which he did not analyse. I therefore decided to examine carefully the action of acid tungstate of potassium.

The paratungstate of potassium which I used was placed in a small porcelain boat in a glass combustion-tube, through which a slow current of hydrogen was passed, at the same time heating to as high a temperature as possible,—in fact, almost to the fusing-point of the glass. The experiment should last about three-quarters of an hour, On breaking the glass tube after cooling, we find in the boat a violet-coloured substance, appearing reddish by reflected light; this is treated successively with boiling water, cold concentrated hydrochloric acid, and a boiling 50 per cent solution of carbonate of potassium, after which it is again washed with hot water. All these washings should be prolonged so that the purification may be complete. This substance occurs in small prisms of a violet-red colour, with a coppery appearance by reflected light; when examined under the microscope these prisms appear to resemble crystals of permanganate of potassium. They certainly seem to be identical with the needles described by Laurent. Their composition corresponds to that of the compound of soda obtained by Wöhler; according to my analyses the formula is—

$$K_2O,WO_3+WO_2,WO_3.$$

		Found. I.	Found. II.	Calculated.
K_2O	..	12·37	11·51	12·14
3W	..	71·36	71·95	71·32
8O	..	—	—	16·54
				100·00

When paratungstate of potassium was submitted to the action of hydrogen at a much lower temperature (dull red) I obtained a mixture of the above-mentioned body, together with a large quantity of binoxide of tungsten and of the blue oxide of tungsten; under these conditions the purification of the product is very difficult.

Finally, by heating the paratungstate of potassium in hydrogen to a bright red heat in a porcelain tube, I found nothing in the boats but very brilliant metallic tungsten. This method of preparing metallic tungsten forms the best means for obtaining it in small quantities.

The results of these experiments show that when we heat paratungstate of potassium in hydrogen, we obtain first, at a low temperature, the blue oxide and the binoxide of tungsten. At a higher temperature *tungsten bronze*, $K_2O.WO_3+WO_2.WO_3$, is formed; it is easy enough to obtain only this compound if we operate at exactly the right temperature. Finally, at a bright red heat, this tungsten bronze is in its turn reduced, giving metallic tungsten.

The action of hydrogen on paratungstate of lithium gave me a different result. Paratungstate of lithium was also distributed in porcelain boats placed in a glass tube and heated in hydrogen for three-quarters of an hour at a temperature approaching the melting-point of glass. After cooling there remained in the boats a brown substance, which was treated successively with boiling water, concentrated hydrochloric acid, and a boiling 20 per cent solution of lithia; the product was then carefully washed with warm water.

In this manner we obtain a brown powder having a metallic coppery appearance by reflected light, composed of very small and completely opaque crystals; under the microscope these crystals have the appearance of octahedra. This is *binoxide of tungsten*; its formula is WO_2.

		Found. I.	Found. II.	Calculated.
W	..	85·35	85·37	85·19
O_2	..	—	—	14·81
				100·00

This method enables us to prepare rapidly large quantites of binoxide of tungsten; the paratungstate of lithium which is used contains 94·89 per cent of tungstic acid. Further, the reduction of paratungstate of lithium by hydrogen gives a pure brown binoxide of tungsten, which is difficult to obtain by reducing tungstic acid in a current of hydrogen at a dull red heat, as is generally done.

By this latter process we do not always obtain a pro-

duct of a constant composition, for, according to the temperature and the duration of the reaction, the reduction may be incomplete, or there may, on the contrary, be a small quantity of metallic tungsten formed.

Binoxide of tungsten prepared by the reduction of paratungstate of lithium is not attacked by hydrochloric acid, or by concentrated alkaline solutions, either hot or cold; we thus see that in the preparation of tungsten bronzes with a potash or soda base, it is absolutely necessary to prevent the formation of this binoxide by working under suitable conditions of temperature.

Paratungstate of lithium, which serves as the primary material for the performance of this operation, is obtained by dissolving tungstic acid in a warm solution of carbonate of lithium, and adding hydrochloric acid until the reaction is slightly acid. On evaporation the solution deposits voluminous plates or rhomboidal prisms, which may be purified by further crystallisation. The extreme solubility and the great deliquescence of these crystals is at first a cause of difficulty, but they can be easily separated from the mother-liquor by using a conical funnel recently invented by M. Tassilly, for drying in a closed vessel bodies which are liable to decomposition by air.—*Bull. Soc. Chim*, 1898, Series 3, vol. xix.-xx., No. 16-17.

THE SPECTRUM ANALYSIS OF NON-CONDUCTING BODIES BY MEANS OF MELTED SALTS.

By A. DE GRAMONT.

In a previous paper, while describing the dissociation spectrum of silicon in melted salts,* I called attention to the fact that the natural silicates, reduced to a fine powder and melted with an alkaline carbonate, give, with the condenser spark, not only the silicon lines, but also the spectra of the bodies which may be combined with them.

A full description of this process and its application to non-conducting minerals, such as silicates, carbonates, oxides, sulphates, &c., will be found in the *Bulletin de la Société Française de Mineralogie*, 1898.

This method gives equally satisfactory results with the insoluble and non-conducting precipitates successively obtained in chemical analysis by the wet way. As in all spectral reactions, the sensitiveness of the test varies with one simple body and another; it is generally better than the blowpipe or wet methods. I therefore thought it would be useful to now give a *résumé* of the parts of this process which can be utilised concurrently with ordinary analysis for examining and checking the precipitates.

A very small quantity of the powdered material suffices, and it does not even need to be dried. It should be intimately mixed in an agate mortar with the salt in which it is intended to be dissolved. A small portion of this mixture is melted in the flame on the flattened end of a thick platinum wire, forming the lower part of the already-described V-shaped connection across the acute angle of which the spark strikes, the two ends being connected to the two poles of the coil and the Leyden jars.

The melted salt used as the igneous solvent of the precipitate should be either carbonate of lithium or of sodium, on account of the simplicity of their spectra. The easy fusibility and superior dissolving power of the lithium salt at a relatively low temperature, causes me to advise its use in all analyses of silicates by igneous disaggregation. The use of other melted salts has been tried. Boric acid and the borates do not give good results; whether melted or in the state of vapour, they form an insulating layer through which the spark strikes with difficulty, giving only the spectrum of platinum (from the wires) and that of the air. Further, the lines of the boron spectrum can only be obtained under quite special conditions, above all with regard to the strength of the spark used. There is therefore no need to use a boron salt as a solvent for other bodies, nor to try and detect boron itself by its dissociation spectrum; it is, on the contrary, necessary to have recourse to the well-known green bands given in the flame by boric acid. We can, however, make use of the alkaline bisulphates for the detection of metals, but a small condensation only—of not more than one jar, for example—must be used, so as to avoid the introduction of the sulphur lines, which would only uselessly complicate the spectrum.

In a case when the nature of the material submitted to examination would give rise to the fear that metallic compounds might be reduced and attack the platinum, the lower spatula should be replaced by a piece of perfectly pure Siberian graphite, hollowed out into a small cup, to contain the melted mixture, and held in the flame by a pair of forceps with platinum points. The source of heat used may be a simple spirit lamp when using carbonate of lithium; with other salts, we must have recourse to the Bunsen burner or a petroleum lamp.

This method has one considerable advantage, viz., the absence of the air spectrum, which does not become manifest until after the complete volatilisation of the melted salt, or when the flame ceases to envelope this latter.

Below are now given some observations on the examination of different simple bodies by the method I have just described:—

Lithium, when tested for with carbonate of sodium, is exceedingly sensitive. When present in very slight traces only, it can be detected by the red line 670·8 and the orange line 610·4. These lines can also be obtained in the cold by allowing the condenser spark to play on a substance containing lithium.

Sodium shows itself by the double Na δ line and the double green Na β, which will indicate the presence of quantities varying from 0·01 to 0·001; the classic double line Na α (D) being always present, either in the melted salt or in the substance under examination.

Potassium, which is not very sensitive to this method, is recognised by its green group K α 583—578, but its violet line 404·6 gives a better reaction.

Rubidium, in traces only, is easily recognised by its two violet lines 421·6 and 420·2.

Cæsium is equally sensitive by its blue lines 459·3 and 455 6.

The alkaline-earthy metals are particularly easy to detect by this method, even in very small quantities. The dissociation of their compounds is easy; further, their arc spectra, studied by Kayser and Runge, are spectra of dissociation, giving the same lines as the condenser spark, as I have verified. It is only the relative intensity of some of the lines that vary within certain limits. We have only to refer to either the original paper by Kayser and Runge ("Ueber die Spectren der Elemente," Berlin, 1891) or to Appendix D of the "Index of Spectra" by Watts (Manchester, 1893) when considering as hardly visible or negligible any lines with an intensity of less than 6 (10 being the maximum). The principal lines, the last to disappear, in their spectra are:—For *calcium*, 445·5, 443·5, and 442·6 in the blue, and especially 422·7 and 396·9 in the violet, and 393·4 in the ultra-violet (these last three lines coincide, as we know, with *g*, H, and K of the solar spectrum); for *strontium*, 460·8 in the blue, 430·6 in the indigo, and 421·6 in the violet; for *barium*, 649·7 and 614·2 in the red and orange, 577·8, 553·6, and 493·4 in the green, and 455·4 in the blue.

Magnesium is characterised by the very sensitive and well known green triplet Mg α 518·4, 517·3, and 516·8; and *glucinum* by the easily seen but decidedly less delicate blue line 457·3.

Manganese is easily recognised by its group of five blue

* *Bull. Soc. Chim.*, 1898, Series 3, vol xix., p. 549. We also find (p. 547, "Spectrum of Carbon") the carbon lines to be deducted from the spectra of the carbonates; in most cases they are reduced to two (657·8 in the red, and 426·7 in the indigo). The lithium and sodium lines in the melted salts are given (*Bull. Soc. Chim.*, 1897, vol. xvii., p. 777).

lines Mn α 482—475. Similarly, *chromium* is characterised by its triple green line 520·9, 520·6, and 520·5; the two latter being difficult to separate with only a moderate dispersion.

Iron and *nickel*, on the contrary, should not be tested for by this method, for even if their lines are not detected, it is by no means safe to conclude that they are not present in the body under examination.

Aluminium, the search for which by means of spectrum analysis is not generally advised, has, on the other hand, given me a very good reaction by its double red line 624·5 and 623·5, slightly diffuse, and almost to be mistaken for a single band. A small quantity of aluminium will show it with great distinctness in the presence of carbonate of lithium, or preferably in this case of a salt of sodium.

Vanadium easily gives its spectrum and shows its presence more especially by a group of strong lines in the indigo, of which the least refrangible 440·8 is the most persistent and the most sensitive; this group extends to 438·0.

Zirconium is easily recognised by its group of five bluish lines, 481·6 to 469; among which 474·0 is the strongest and the last to disappear.

I will not now speak of the line spectra of the metalloids, which have already been described in my researches on dissociation spectra. I will only mention that their sensitiveness, which is very marked in compounds in which they are not combined with oxygen—such as sulphides, selenides, tellurides, chlorides, iodides, and bromides—becomes, on the contrary, comparatively faint in the corresponding oxy-salts, whose dissociation requires a strong condensation (4 to 6 jars) before the lines of the metalloids appear. In such a case, the use of carbonate of soda appears to me to give better results than carbonate of lithium.

The arrangement of the apparatus and the manner of making observations are the same that I have all along used in the examination of melted salts. The spectra obtained are the elementary spectra of the same species, and the greater number of the simpler bodies give satisfactory results by this method.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., Nos. 16-17, 1898.

ON THE

VOLUMETRIC ESTIMATION OF COMBINED SULPHURIC ACID.

By MM. F. MARBOUTIN and M. MOLINIÉ.

We have already pointed out a method for this estimation (*Bull. Soc. Chim.*, Series 3, 1897, vol. xvii., p. 953), based on the precipitation of the sulphuric acid in the state of sulphate of barium, the barium remaining in solution being itself precipitated by an excess of chromate of potassium of which the unused portion was titrated by arsenious acid and iodine, the difference in the results obtained, when operating on a sample for analysis and on distilled water, giving the proportion of SO_3 present.

The use of standard solutions does away with many causes of error, simplifies the preparation of the solutions of which one only (iodine) is titrated, and makes it possible to work in a satisfactory manner with materials of doubtful purity.

Several writers (H. Pellet, *Bull. Soc. Chim.*, 1876, vol. ii., p. 251; F. Mohr and Classen, "Traité d'Analyse par Liqueurs Titrées"; Windisch, *Moniteur Scientifique*, 1895, p. 301), and more recently M. Telle (*Journ. de Pharm. et de Chim.*, Feb., 1898), and M. Robin (*Ibid.*, March, 1898), advise the use of equivalent solutions of potassic chromate and chloride of barium. This method, though very enticing at first sight, since the chromium remaining should be mathematically equivalent to the sulphuric acid precipitated, does not appear to us to have that degree of accuracy that the chemist of to-day expects from his analyses.

Without laying too much stress on the uncertainty of the atomic weights of barium and of chromium, the solubility alone of the chromate of barium may easily be the cause of errors, often very considerable.

By taking 137·2 as the atomic weight of barium, and 52·4 as that of chromium, we have observed that in precipitating equal volumes of *so-called* equivalent solutions, in the neutral state, the clear decanted liquid *always contained both barium and chromium*. The amount of chromium was found to be equivalent to 1·5 m.grms. of sulphuric anhydride in 50 c.c. of decinormal solution: this figure, which may appear to be insignificant, becomes of great importance if we compare it with the quantity of sulphuric anhydride contained in the sample taken (10 to 15 m.grms. at the most). We may thus make an error of 10 per cent excess in an estimation by direct reading. The use of a standard solution enables us to make a correction for this error, the amount of chromate of barium going into solution not influencing the results given by the difference between the two readings in any way.—*Bull. Soc. Chim.*, Series 3, vol. xix.-xx., No. 15.

SUPPLEMENTARY NOTE.—The method for the volumetric estimation of combined sulphuric acid which we have just described is applicable to waters containing only a small quantity of organic matter (springs, rivers, wells). This method can, however, be easily extended to sewages, waste waters, cesspools, &c., after a preliminary treatment for the purpose of eliminating the organic matter such waters contain.

This destruction is effected preferably by fuming nitric acid charged with nitrous vapours. Our method of operating consists in slowly evaporating 200 c.c. of the water under examination with 20 drops of nitric acid on a sand-bath. The cold residue treated with fuming nitric acid is evaporated to dryness. The excess of acid is driven off in the presence of hydrochloric acid; we take up with water, and the clear liquid is submitted to the process already described (*Bull. Soc. Chim.*, Series 3, 1897, vol. xvii., p. 953).

We have thus obtained the results given in Table I.

The variation between the results obtained are only what may be classed as errors of experiment, the limit being 1 m.grm. per litre.

We tried the beautiful reactions given by MM. Villiers (*Comptes Rendus*, 1897, vol. cxxiv., p. 1457) and Lindet (*Ibid.*, 1897, vol. cxxv., p. 246) for the destruction of the organic matters,—that is to say, the use of nitric acid in the presence of a salt of manganese or of vanadium. The estimations made were very satisfactory. The

TABLE I.

Origin.	Estimation by weight.				Estimation by volume.					
	Organic matter.*	Sample taken.	Weight of $BaSO_4$.	SO_3 per litre.	Sample taken.	Standard.	Reading.	Difference.	Values of I in SO_3.	SO_3 per litre.
	M.grms.	C.c.	M.grms.	M.grms.	C.c.	C.c.	C.c.	C.c.	M.grms.	M.grms.
Biévre	39·0	200	193·3	331·6	50	24·85	14·20	10·65	1·5537	331·0
Collector at Asnières	39·4	200	51·8	88·9	50	22·65	19·85	2·80	1·6012	89·7

* The organic matter is expressed by the weight of oxygen (in m.grms.) furnished by alkaline permanganate of potash, to oxidise 1 litre of water.

destruction of the organic matters is in this case *much more rapid* than with nitric acid only; the solutions thus prepared are very convenient for the estimation by weight.

TABLE II.

Origin.	SO_3 per litre after treatment with nitric acid. Alone.	With chloride of vanadium.	With chloride of manganese.
	M.grms.	M.grms.	M.grms.
Bièvre	331·6	329 6	332·0
Collector at Asnières	88·9	89·7	89·4

But though the vanadium and manganese remaining do not cause any error in the gravimetric estimation, such is not the case with the volumetric estimation, for which we prefer the use of nitric acid only.

Many writers advise letting the liquid from which we have just precipitated the sulphuric acid by chloride of barium stand for a time in a warm place. We have examined the practical influence of the duration of this digestion on the estimation.

TABLE III.

Samples.	Weight of sulphate of barium precipitated after— 10 mins.	1 hour.	2 hours.	12 hours.	Differences. Maxima.
	M.grms.	M.grms.	M.grms.	M.grms.	M.grm.
No. 1	297·8	297·5	297·3	297·9	0·6
„ 2	118·6	118·6	—	118·8	0·2
„ 3	58·4	—	—	58·1	0·3
„ 4	30·4	—	—	30·8	0·4
„ 5	13·0	—	—	13·4	0·4
Well water ..	216·0	—	—	216·5	0·5
Water from collector ..	52·2	—	—	52·0	0·2

The differences obtained can only be classed as errors of experiment; they do not exceed 0·6 m.grm. of sulphate of barium, or 0·17 m.grm. of sulphuric anhydride, in the sample taken.

But though the duration of the digestion does not appear to influence the results, this duration has an important action on the manner in which the precipitate is agglomerated. Such a cooling, as slow as possible, of a boiling liquid in which the sulphuric acid is precipitated is one of the essential conditions of an easy and quick filtration: we have therefore adopted the plan of digesting for twelve hours at about 40° for gravimetric estimations. For volumetric estimations the final precipitation of the excess of barium by chromate of potassium clears the liquid to a certain extent, the clear portion only being used, so that we have been able to dispense with this long digestion, and thus greatly shorten the time of the operation.—*Bull. Soc. Chim*, Series 3, vol. xix.-xx., No, 15.

The Composition of Phosphorescent Sulphide of Strontium.—J. R. Mourelo.—The author obtains the most phosphorescent compound by treating a large quantity of strontium carbonate with some sodium carbonate and sodium chloride at a red heat. The mass obtained is then mixed with sulphur and bismuth subnitrate, and heated for four hours at a bright red heat. The product gives an intense phosphorescence. Analysis shows that it contains—besides strontium sulphide—sodium and bismuth sulphide, sodium chloride, and traces of bismuth oxide, and sodium sulphate, in addition to varying quantities of strontium sulphate. Experiment shows that the bismuth is really the active agent when in the form of subnitrate, but its activity is only developed in the presence of compounds of the alkalis. The best results were obtained by using 2 grms. of sub-nitrate of bismuth, 100 grms. of strontium carbonate, 2 grms. of sodium carbonate, and 0·12 of sodium chloride.—*Comptes Rendus*, cxxvii., No. 8.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE BANQUET TO PAST PRESIDENTS.

Professor DEWAR, F.R.S., President, in the Chair.

(Continued from p. 276).

PROFESSOR ODLING—"I do not know that I can better commence the few observations I propose to make to you than by following in the wake of my predecessor, Sir Edward Frankland, and saying that it is no less a great pleasure than my bounden duty to express to you, Mr. President, and to the Council and Fellows of the Society, my heartfelt thanks for the great compliment that you have paid to my colleagues and myself on this long-to-be-remembered occasion. Speaking, however, for myself personally, it is not the first time that I have had evidenced to me the kindly feeling of the Chemical Society. On the occasion of my retirement from the Secretaryship in 1869, I had also the special honour done me of being entertained at a dinner by the Society; and I also received a further token of their good will in the form of a capacious loving cup of no inconsiderable value in itself, but of far greater value as a perpetual mark of the kind feeling towards me of those with whom I had been for so many years so intimately connected. Those of us whom you entertain this evening have for a long period of time, as Sir Henry Gilbert and Sir Edward Frankland have already remarked, been associated with one another in common pursuits and enjoyments; and if there is one thing more than another that enhances to me the gratification of this meeting, it is the pleasure of finding myself associated still with my old friends and colleagues, Gilbert and Frankland and Williamson and Gladstone, and my earliest friend of all, Sir Frederick Abel. We have been concerned with one another in a large number of undertakings, and for a long period of time have been accustomed to hear one another's voices as well upon festive as upon scientific occasions. But we have not been accustomed to hear them in exactly the order they have been arranged for this evening. I have always looked upon myself, not as a precursor, but as a follower of Wiliamson. It has been my pride to reckon myself one of his adopted pupils—a disciple of his ideas more perhaps than many of those who were his actual pupils. He was always very decided in his notions. Sometimes, indeed, I turned a little restive, but was always soon pulled up into form again—sometimes more abruptly, perhaps, than was quite agreeable at the moment. At one time I laboured under the sad suspicion of being a little unsound as to the Atomic Theory. Well, perhaps I was not altogether so stalwart in its defence as I ought to have been; but I can assure you that I was never really guilty of so reprehensible a heresy as that which was attributed to me.

"You are doing us honour here this evening not so much, or not only, as students of the science of chemistry, but also as Past-Presidents of the Chemical Society. As ancients of that Society, we may all of us perhaps be permitted to talk a little about ourselves without incurring the imputation of egoism, and also to talk a little about old times without incurring the reproach, after our fifty years' fellowship, of senile garrulity. At the period during which I acted as one of the Secretaries of the Society, and my colleague, Professor Redwood, concerned himself mostly with the business department of our affairs, the Chemical Society had not developed very far its function as a publishing agency, and as a consequence—even for that little prolific time—we did not get our fair share of important papers communicated at first hand to our meetings. But if we did not receive elaborate communications, we enjoyed the benefit of elaborate discussions; and there was no new class of compounds, no newly propounded doctrine, no new reaction which was

not submitted to our keen examination and controversy. The subjects of several of those controversies, and even the fashion of them, still linger in one's memory. I need scarcely say that chemical theory came in for a large share of our attention. The molecular weights of water and carbonic acid, the atomic weights of oxygen and carbon, and, above all, the then newly introduced idea of polyatomic radicles, were keenly discussed. We were a little too late for the interesting question as to whether compound radicles could possibly be oxygenous; but still radicles were predominant at that time in chemical science, and reigned with undisputed sway over the whole domain of organic chemistry. One cannot but reflect how fleeting has been their reign. The doctrine of radicles has now sunk to an entirely subordinate position in chemistry, not unlike, may I venture to say, the subordinate position into which radical doctrines have fallen in a different sphere. There was one particular controversy I remember very well, and am sure Frankland will remember also. It was of this kind: whether the bodies called ethyl and methyl were really ethyl and methyl at all, or something else. Well, a question of that kind in those unsophisticated days had to be answered definitely by a plain aye or no. There was no loophole for escape or trimming, no possibility of saying that the one answer was just as true as the other, according to the point of view taken; nor was there existent in that period of innocence, for the solution of yet more puzzling problems, what we know now by the name of tautomerism, by which we learn that a body is, and at the same time is not, what it is alleged to be; that it is sometimes one thing and sometimes another, and sometimes both together, and yet preserves its individual chemical entity. In those days the principal provider of chemical material for our meetings was far and away Hofmann. He was in the habit of sending his multitudinous papers to the Royal Society for publication; but he gave us the advantage of his presence and his personal disquisitions; and I would appeal to all in this room who had the advantage of seeing him, to say if they can possibly forget his appearances at the blackboard of the Chemical Society, and the enthusiasm and lucidity of his expositions of different points of chemical constitution, enlivened as they were by that extraordinary display of vivacity so inconsistent with the quiet phlegm we are in the habit of attributing to those of his nationality. But, despite the productiveness of Hofmann, still there were evenings on which something else was required; and then it behoved the Secretary to search far and wide for material to bring before the meeting of chemists who, with Greek like avidity, were always clamorous for 'some new thing.' At that period the activity of the Giessen school was somewhat on the decline, and we loooked for novelties in chemistry, as for novelies in mantles and millinery, to Paris. We had for our consideration the acidic ammonias of Gerhardt and the diatomic glycols of Wurtz, and the production of alcohol without the aid of either sugar or yeast by Berthelot, and many other remarkable contributions to the knowledge of the day. But our friends across the water, with so much—so very much—justly due to them, nevertheless did manifest now and then a tendency to appropriate to themselves what did not altogether belong to them; and in this, the country of Black and Priestley and Cavendish and Dalton and Davy, we were astonished one fine morning at being informed that 'la Chimie est une science française.' But even with the productiveness of Hofmann and the searchings of the Secretary, it did sometimes happen that our bill of fare was a little meagre. But what of that? Those were supper-eating days, and a meeting rendered brief by want of pabulum could always be supplemented by a prolonged and substantial, and, I may add, a musical, meal at a then well-known resort not far from Covent Garden; and when it happened, as it did sometimes, that our proceedings were not so exhilarating as they should have been, when divine philosophy had proved less charming than its wont, Hofmann, despite the abundant supply of tea and coffee of excellent quality, would, with a burst of inspiration, thrust forth his right hand, and say 'I will tell you, we will have a punch!'

"But the Chemical Society has a future to look forward to, as well as a past to look back upon. At the Jubilee of the Society some seven or eight years ago, it devolved upon me to give an account within the short period of a quarter of an hour—I believe I occupied twenty minutes—of the progress of chemical science during the preceding fifty years. But to-day is also a Jubilee, or almost so, the Jubilee of our incorporation by Royal Charter, which, in the then days of our insignificance, Playfair did so much to obtain for us. Now, on this diamond Jubilee, I ask you how many minutes will you give me to lay before you a forecast of the chemical progress that may be expected to take place within the next fifty years? I will only venture to say that, judging by the number and activity and intellectual gifts of the workers of the present day, we may feel assured that the achievements of English chemistry and the progress of the Chemical Society in the past, will be as a mere nothing to the brilliancy to which they will attain in the future."

Sir Frederick Abel—"Sir Edward Frankland has out of his vast stores of knowledge recalled a fact of which I confess I was ignorant, that in years past I indulged a poetic fancy. I only wish I might now be inspired in order to find words to express on behalf of myself and my old friends our appreciation of this glorious reception which you have given us. The Chemical Society is endeared to me in many ways. Among the epochs of a somewhat long career of ceaseless activity, that which connected me intimately with the work of the Society is one of those which I recall with the greatest pleasure and satisfaction. And it so happens that the years of my connection with the Society in various functions were years in which some of the most memorable events in its annals occurred. As Treasurer, it was my privilege to arrange with the illustrious chemist and brilliant orator, Jean Baptiste Dumas, for the delivery of the first of those memorable lectures which were given through the agency of the Chemical Society in honour of the memory of Michael Faraday. While I was Treasurer, the volume of the Journal of the Society, which was then of modest and slender dimensions, nurtured by well-digested extracts from foreign journals, speedily gained proportions unwieldy in character, so unwieldy, in fact, that the one volume split up into two before long. In the first year of my Presidency, the Research Fund, which was initiated in a modest manner by Mr. Thomas Hyde Hills, was placed upon a firm and substantial basis through the generosity of one of the most respected of the Society's original members, Dr. Longstaff; and in the second year in which I held that office, the somewhat revolutionary agitation which was persisted in by a not unimportant section of the younger Fellows of the Society,—an agitation which, by the way, has been imitated since,—led to earnest deliberation and consultation between the Council and some of its chosen members outside the Council, which resulted in the birth of an institution now flourishing exceedingly, which has become the guardian of the best interests not only of the chemical profession but also of the public. I of course allude to the Institute of Chemistry of Great Britain and Ireland. When I look back to the early days when I first owned the proud title of F.C.S., and remember my attendance, in a small room at the Society of Arts, at the meetings of the Chemical Society, presided over in succession by William Brande and Phillips, the business being managed by George Fownes and Robert Warington, the founder of the Chemical Society, and the funds not very cleverly handled by dear old Robert Porrett, one of the most prominent forms that appears in my mind's eye is that of the favourite pupil of Liebig, my venerated master, Hofmann. In the very first years of the Society, Hofmann became the very life and soul of it. He was beloved by his English brethren directly he came

among them, and for years he was by far the most prolific contributor, either himself or through his pupils, to the volumes of the Society. Pardon me if I have been tempted into reminiscences; it is difficult to avoid it at such a gathering as this. The welcome you have given to the veteran Past-Presidents will remain in their minds to their last day as one of the great joys of their lives. To the many old friends and colleagues whom I see around me—Past-Presidents who, as men of science, hold positions second to none, whose names are familiar as household words—to them I can wish no higher gratification than that they may live to experience the satisfaction of such an entertainment, and of such a graceful appreciation of their work, as has been the lot of your old Past-Presidents to-night."

Professor A. W. Williamson—"I thank you, Mr. President, most heartily for the kindly words you have uttered in relation to me and to my efforts for the advancement of chemistry. It is an immense satisfaction to me to see a man of your talents and vast acquirements placed in so influential a position as that which you so worthily occupy. But whilst thanking you I am bound to confess that I have been for some time past a most unworthy member of the Chemical Society. It happened that after a good many years of work in our Society, I had other matters of such importance claiming my time and attention, that I was unable to continue to work amongst my colleagues and friends in the Chemical Society.

"Before I came over in 1849 to work at University College, I had become acquainted in the Giessen Laboratory with that most remarkable man August Wilhelm Hofmann, and I may mention a characteristic incident illustrating his earnest and steadfast devotion to his science. He had for a considerable time been working at derivatives of aniline, and in order to carry on these researches as effectively as possible, he prepared by the action of caustic potash on indigo about some two gallons of aniline. The product was placed in a big bottle on the mantelpiece in his bedroom, and the story goes that he used to stand and gaze at it for some time every morning and evening, and gloating over it with delight would think 'What a number of splendid products I shall make out of this aniline!' The energy and devotion with which he followed up his work on the derivatives of aniline, at the expense of many other researches which he might with advantage have followed up, was such that he came to be talked of as the great worker on aniline, and Sir Benjamin Brodie somewhat prematurely wrote his epitaph in the following words: 'Hic jacet Aniline.' His researches extended, however, at an increasing rate into other and wider departments of chemistry, and his energy and enthusiasm were such as to make him the leading explorer in the domain of organic chemistry. Berzelius had been for a lengthened period the one great man in the domain of inorganic chemistry, which was the only part of the science which had been explored to any appreciable extent. When I saw the vast piles of knowledge which Hofmann was so rapidly accumulating in the new domain of chemistry, I felt, and ventured to say, that his masterly labours entitled him to be called the Berzelius of Organic Chemistry. I happened to be present at a meeting of the Chemical Society at which a young chemist read a paper in the presence of Hofmann on some theoretical matters of importance which had already engaged the attention of distinguished chemists. Hofmann did not enter into any particulars of the paper, but he gave vent to an outburst of heartfelt delight at the simple narrative which had been read. There are various incentives to work, but the most potent incentive to earnest and efficient work is probably the example of a man like Hofmann, whose whole delight lay in mastering the truths of science, and in learning more and more particulars of the order of Nature, and Hofmann possesssed that power in a most eminent degree.

"We see in this grand hall an assemblage of chemists known by their earnest labours and valuable discoveries, and we are honoured by the presence of men of the highest distinction in other branches of science, as well as of leaders in the learned professions. It might not be unreasonable to believe that enthusiastic delight in the triumphs of chemical research is duly represented by some of the guests in this hall, and that the lively conversation which has been going on may not relate merely to high questions in jurisprudence, medicine, or legislation, but that some samples of chemical enthusiasm may reach the ears of the learned representatives of other professions.

"I feel sure that at a future time we shall all look back with the highest pleasure upon this delightful evening, which we owe to the kindly exertions of our President and other leading members of the Society.

Dr. John Hall Gladstone—"It is a pleasant thing to look on the faces of so many friends with whom one has worked in olden times, with whose works one is well acquainted; though, of course, there are many at the present time who come into the Society, and whom I can look to as budding philosophers: unfortunately, I do not know their names so well as their faces. The pleasure is not merely because we call ourselves chemists, but because there is a bond of union between us arising from the desire of discovering the wonderful secrets of the great cosmos of which we ourselves form part. There is a great difficulty in speaking to you this evening, because so much that I should have liked to say has already been said by previous speakers. Still there are one or two things which, if you will permit me, I should like to bring before you. First of all, in your too flattering description of myself and of my work—which makes me rather ashamed to stand up and speak—there was a point which I think calls for remark, and so I must venture upon that which characterises the speeches of all of us, a certain amount of early autobiography. I was exceedingly fond of science from a little child. My favourite science was geology, and also what could be seen in the microscope—infusoria, and other little objects we have heard of in later times. But, in choosing a profession, my father said geology was not a promising career, and recommended chemistry. I knew very little about it, but went to University College and studied under that admirable teacher Professor Graham, and afterwards under Liebig. I suppose it was from Graham that I acquired the taste for the physical side of chemistry and its connection with heat, light, electricity, and other forces of nature. I looked out for a scientific position, and lectured at St. Thomas's Hospital for some time, made analyses, and considered myself a professional chemist. It may be that circumstances have caused me to sink into the position of an amateur chemist, but my first intention was that of following chemistry as my profession in life. It has not been necessary to continue that; and I have had this advantage, that I could always keep in my laboratory a good trained assistant, and thus, whilst I was engaged in other works and ways, and in endeavouring to extend the knowledge of chemistry and elementary science in our primary schools, the work still went on more or less under my immediate direction. I should have liked to have said something about the progress of chemistry during these past fifty years; but the subject is so enormous, and you yourself have touched upon it to such an extent and so well, that I need only allude to the fact that this great change of volume of chemistry has caused it to be necessary that we should specialise. Specialisation has its advantages, but also its disadvantages. One danger is that we may become narrowed in our views. So it would appear best to have a home somewhere or other, but to make occasional excursions in the neighbourhood, and take summer holidays so as to get our nerves braced up to work again at our own pet subjects. I must not touch upon other points, such as the relations of the physical forces to chemistry, or its useful applications, and the great value of chemical research for the welfare

of mankind. These are subjects too large and important to enter upon at this late hour. It seems to me that while we are always increasing the mass of knowledge we possess, the space which we see to be bright becomes larger and larger, but there is beyond a dim nebulosity. It is our work to bring from that nebulosity something into the bright space, so that it becomes the property of the human race. But there is beyond this a region which we do not understand—infinite as far as we know—and our object is to increase that which is knowable, in the firm belief that it will be for the advantage of our fellow creatures. While I feel thankful for the joy that I have had in taking some part in these discoveries, I cannot look to have much more time given me for carrying on this work of investigation; but still there may be a few threads of old research I may gather up, and in doing so I shall be greatly encouraged by the kind remarks of this evening, and the way in which our work has been received by the friends gathered around us."

(To be continued).

NOTICES OF BOOKS.

Report of the Senior Analyst of the Cape of Good Hope for the Year 1897. Cape Town: W. A. Richards and Sons. 1898. Pp. 88.

The number of articles analysed during the past year, though slightly in excess of that of 1896, is still rather less than in 1895. This decrease is attributed to a change which has been effected in the administration of the Adulteration Act. The number of samples examined in 1897 was 979, and consists of every variety of substance; milk and water being the most frequently done. Supposed gold ores show a considerable falling off, the numbers being 44 in 1896 against 27 in 1897; while there are no less than 28 new substances in the list which were not previously dealt with, such as condensed milk, bread, honey, rice, glycerin, quinine wine, henbane, zinc, &c. The money value of the analyses made was £1270 4s. 9d., being an increase of about £150 over that of any previous year.

Of 549 samples of foods examined, 104 were found to be adulterated, the chief offenders being milk (fresh and condensed), coffee, and brandy; but it is satisfactory to note that the proportion of adulterated articles has fallen from 30 per cent in 1894 to only 19 per cent in 1897 of the total number examined.

Forty-four samples of water have been analysed during the year. We are, however, surprised to read that an analysis of water from the Table Mountain reservoirs contained as much as 5·46 grains of organic matter per gallon; surely this must be a misprint, the total solids are only 9·24 grains per gallon.

A large number of analyses have been made of soils and manures, an important subject for an agricultural colony like the Cape of Good Hope, and a number of maps, diagrams, and curves showing the results are to be found at the end of the report. It is, however, proposed to suspend these investigations for awhile in order to devote time to other more important agricultural questions.

Thirty-fourth Annual Report on Alkali, &c., Works. By The Chief Inspector. Proceedings during the Year 1897. London: Eyre and Spottiswoode. 1898. Pp. 129.

Since the publication of the last Report, Sub-Inspector Mr. B. E. Smith has resigned his position, which has been filled by the appointment of Mr. J. W. Young, B.Sc., who will take charge of No. 2 District, comprising the northern counties of England.

The number of works now registered under the Acts in England, Ireland, and Wales is 1058; of these, only 87 are works decomposing salt, and therefore described as alkali works, while the remaining 971 are scheduled under the Acts of 1881 and 1892. These figures show a decrease of 11 alkali works and 5 other works since 1896. There are also 125 works registered in Scotland, bringing the total number up to 1183.

The total number of visits made in England, Ireland, and Wales during the year was 4116, and 4562 tests were made. It must, however, be borne in mind that no figures are given regarding No. 2 District, and that one of the inspectors was incapacitated for ten months owing to a serious accident, otherwise these numbers would have been considerably larger.

It is very satisfactory to see that there have only been three prosecutions under the Act, and that these were not very serious cases.

The number of works using the Leblanc process shows a reduction. Nevertheless, great activity is displayed in those works remaining in operation, requiring close attention from the inspectors.

Reviewing the industry as a whole, the Chief Inspector states that he has every reason to be satisfied with the care displayed and the competence shown by the management, so that in no single case has the question of prosecution for infraction of the Act assumed a serious shape; complaints of damage to crops have almost ceased. The effect of sulphide of calcium in presence of iron salts in sewage as a germicide has received some attention at the St. Helens sewage works.

It has been also noticed that the vapours evolved on the running off of pitch are so highly valued as a remedy for children suffering from whooping cough that, by permission of the owners, many patients were sent to the works to inhale the vapours given off during the progress of the operation. It is also pointed out that, during epidemics of infectious diseases, the cases notified within the chemical work's area were always lower than in other districts; while the general death-rate per 1000 is as 16·6 to 10 in favour of the chemical work's area in 1893, and 14·4 to 9·2 in 1896.

The reports from the different sub-inspectors fill a large portion of the book, close details and tabulated results being given of the work done during the year.

Report of the Chemist at the Central Experimental Farm, Canada. By F. T. Shutt, M.A., F.C.S. 1896. Author's Edition. Ottawa: Government Printing Office. 1897.

The matter here reported on is briefly outlined under the headings of Soils, Mucks and Muds, Manures and Fertilisers, Fodders, Waters, and such like.

We are sorry to see that there was a disastrous fire in the laboratory in July, caused by the accidental bursting of a flask of boiling sulphuric acid. Nearly all the apparatus was destroyed, but the greatest loss was in samples and records—the accumulation of nine years' work.

Some instructive results obtained by fermenting manure for one year in a shed are given. They show that there was a considerable loss of fertilising constituents during that period. Finely-ground mineral phosphate was mixed with strongly fermenting manure, but the results showed that practically no phosphoric acid was thereby made available.

As in past years, the analysis of well waters from farm homesteads has been continued, the results showing plainly that in many cases polluted water is being used, 45 per cent of the samples were very seriously polluted, 20 per cent were suspicious and probably unsafe, while only 35 per cent were returned as wholesome and fit for use.

Lectures on Physical Chemistry. Delivered at the University of Berlin by J. H. van 't Hoff. ("Leçons de Chimie Physique Professées a l'Université de Berlin"). Translated from the German (into French) by M. Corvisy. Paris: A. Hermann.

This volume is devoted chiefly to a consideration of "Chemical Equilibrium"; that is, to the limiting conditions in which chemical bodies can exist in stable equilibrium.

Starting with the simple examples—"Water" (which can, at suitable temperatures and pressures, exist in two or three forms in contact) and "Sulphur" (which can similarly exist in two, three, or four forms)—the Professor goes on to discuss the more complex cases of a salt in solution (where concentration enters as a condition), then of two salts (which may or may not have a common base, and in which double decomposition may or may not take place).

The conditions of stable equilibrium are expressed in simple formulæ, involving a slight acquaintance with the calculus, based upon the laws of Boyle, Gay-Lussac, Avogadro, and others.

These simple reactions have been well worked out by many observers, and it is interesting to note the close numerical agreement between the theoretical and observed results.

The formulæ are also applied to more complex reactions still, and a certain measure of agreement, though not so close as before, found between the theoretical and the scanty experimental results.

Section II. is concerned with the rate at which chemical reactions take place, and with the mechanical and electrical measurement of the force of affinity between different molecules. The various causes which modify the rapidity of a reaction are considered one by one, and the laws governing them set forth. The effects of pressure, temperature, and dilution are clearly marked, but the effect of the wave propagated in an explosive mixture of gases is still undecided; various empirical formulæ have been suggested, but they do not in any case fit more than two or three of a series of experimental results.

The volume is a valuable contribution to the records of modern scientific research.

CORRESPONDENCE.

THE PROPERTIES OF LIQUID MIXTURES.

To the Editor of the Chemical News.

Sir,—In the abstract of my communication to the Physical Society, in connection with Mr. R. A. Lehfeldt's paper on the above subject (Chem. News, lxxviii., p. 276), the most probable explanation of the fact that, when American petroleum is distilled, the benzene comes over at about 65° instead of 80°, is stated to be that "benzene and hexane behave, as regards distillation, *like miscible liquids.*"

This should read "*like partially miscible liquids.*"

The two liquids are, in fact, miscible in all proportions, and the point is that, in certain respects, they behave as though they were only partially miscible.—I am, &c.,

Sydney Young.

University College, Bristol.
December 6, 1898.

THE GASES OF THE ATMOSPHERE.

To the Editor of the Chemical News.

Sir,—If your readers could not expect Professor Ramsay to reply to my last letter, I am sure they were yet further from expecting Professor Tilden to rush in where that angel feared to tread.

Agreement is always delightful, therefore I am happy to agree with Professor Tilden in thinking that chemists have heard enough about the respective shares of Lord Rayleigh and Professor Ramsay in the discovery of argon. Unfortunately, Professor Ramsay is of a different opinion, and is constantly endeavouring to alter the distribution to his own advantage. It would no doubt suit him very well to see these efforts passed *sub silentio.*

In my last letter I showed that Lord Rayleigh and Professor Ramsay have given entirely different accounts of the same simple occurrences. I quoted the two narrations so that everyone could see for himself. Professor Tilden apparently cannot see; and it might aid him were you to print the thing in parallel columns, thus:—

Lord Rayleigh	*Professor Ramsay*
Said, in 1895, that his own researches suggested to him the question whether the so-called nitrogen of the air is all of one quality.	Says, in 1898, that it was he who suggested this question to Lord Rayleigh.
That he propounded this question to Professor Dewar, who referred him to the Cavendish experiment made a century before.	That it was he who directed Lord Rayleigh's attention to the work of Cavendish.
That when the suggestion was made to him, he at once saw its importance, and quickly followed it out, finding that Cavendish had put the same question as himself.	That Lord Rayleigh did not at first attach much importance to the suggestion, and thought it more likely that different compounds contained different kinds of nitrogen.
Wrote a letter to *Nature* on September 25, which was published on September 29, 1892.	Says that this letter appeared early in 1894, and that it was the immediate cause of his entering into the field at that date.

Here we have three categorical statements made in public by Professor Ramsay which are irreconcilably opposed to Lord Rayleigh's lucid and straightforward narration, and a fourth statement which a reference to *Nature* shows to be incorrect. Two of these statements are in disparagement of Lord Rayleigh, one in disparagement of Professor Dewar, and all four are intended to glorify Professor Ramsay at their expense. This is the case which Professor Tilden ought to have been prepared to deal with when he entered the arena. The issues, be it observed, are simple questions of historical accuracy depending upon ascertainable facts and the relative credibility of different witnesses.

Professor Tilden has not dealt with the case at all. His nearest approach to dealing with it is a sorry quibble relating to one point out of the four. He asks how I am to know what conversations Lord Rayleigh had with chemists, or how many of them mentioned the Cavendish experiment to him. I do not know, nor do I care in the least; a dozen men may have referred to Cavendish in conversation, but only one man can have "directed his attention" to the Cavendish experiment or told him anything about it which he did not already know. Lord Rayleigh says that Professor Dewar was the man who did him this service. Professor Ramsay says that he was the man. I believe Lord Rayleigh: first, because he has never been known to say the thing that was not; and second, because he is the only man living who can speak with absolute certainty upon the point. Professor Tilden prefers to believe Professor Ramsay. That only proves what is abundantly evident from the rest of his letter—that Professor Tilden does not cultivate the scientific habit of mind.

For the rest of his letter is wholly irrelevant. It is composed of an imputation of malice, a sniff at anonymity, a superfluous certificate of character and reputation to Lord Rayleigh, an absurd attempt to infer his private senti-

ments from his remarks upon an occasion when their obtrusion would have been an offence against good taste, and—worst of all—a most lamentable exhibition of incapacity to understand how a gentleman would act if in an official capacity he had to deal with the case of a man with whom he had a private difference. Quite as a matter of course, Professor Tilden bases an argument upon the tacit assumption that if Lord Rayleigh had felt privately aggrieved by Professor Ramsay, he would have used his influence as an official of the Royal Society to prevent the bestowal of the Davy Medal. In the case supposed, I am convinced that Lord Rayleigh's conduct would have been of a diametrically opposite character. From this argument I infer that Professor Tilden is even less than myself in the confidence of Lord Rayleigh.

For the sake of clearness—it seems impossible to be clear enough for some people—I will repeat that the first and third points upon which Professor Ramsay flatly contradicts Lord Rayleigh are not met by his apologist in any way. One contradiction represents Lord Rayleigh as incompetent to draw an obvious inference from his own work without the assistance of Professor Ramsay. The other represents him as too dull to see the value of a suggestion coming from the same "universal provider," who we must infer kindly carried on Lord Rayleigh's education until the importance of the Cavendish experiment at length dawned upon him. On the fourth point, the mistake as to the date of Lord Rayleigh's letter to *Nature*, Professor Tilden has not a word to say. Most significant of all, he shirks entirely the damaging conclusions which I drew from the whole case, and the challenge for the production of evidence in support of assertions. When the eminent authority upon science and morals, or his apologists, shall have fairly faced and disposed of the awkward facts of the case, instead of dealing in ridiculously inept inferences concerning Lord Rayleigh's private sentiments, I fancy they will have little stomach left for inquiring into the motives or the personality of—Yours, &c.,

Suum Cuique.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 8, August 22, 1898.

Oxides of Sodium.—M. de Forcrand.—The author studies the products of the direct combustion of sodium in dry air free from carbon dioxide. The experiments take place in a small retort attached to a large globe, through which passes a slow current of air. Slightly below its fusing-point, the sodium becomes covered with a grey layer, which soon increases in volume if the experiment is stopped at this point. If, however, the heating is continued, the grey substance ignites in the current of air, and the vivid combustion is accompanied by two phenomena:—(1) White vapours are produced, which are very volatile and condense only in small quantities in the retort and globe. (2) As the grey substance burns, it is transformed into a yellowish substance, which becomes nearly white on cooling. These products are examined and analysed. The grey substance formed at first has the composition Na_3O; the white volatile powder, Na_2O_2; and the white substance, which is yellowish when hot, is a mixture or Na_2O_2 and Na_2O. Na_2O_3 is not formed by this method.

Ammoniacal Chlorides of Lithium.—J. Bonnefoi.—The author investigates the four possible combinations of lithium chloride and ammonia. $LiCl.NH_3$ is formed when LiCl absorbs quite pure and dry NH_3 at temperatures above 85° and atmospheric pressure; the compound formed being kept above 85°. $LiCl.2NH_3$ is formed under the same conditions between 60° and 85°. $LiCl.3NH_3$, between 20° and 60°; and $LiCl.4NH_3$, the saturated compound, below 13°. Measurements show that the heat of combination diminishes in proportion as the new molecules are added; while, at the same time, the stability of the compound diminishes, and the dissociation tension becomes greater for the same temperature. The numbers for the heat formation, calculated by Clapeyron's formula, agree in all cases with the direct thermo-chemical measurements.

No. 9, August 29, 1898.

This issue contains no chemical matter.

No. 10, September 5, 1898.

Silicide of Tungsten.—E. Vigouroux.—Moissan has determined that silicon and tungsten combine if heated together in the electric furnace. The author investigates the properties of the substance formed. He heats together silicon and tungsten oxide, obtaining a heavy whitish mass. To obtain from this the tungsten silicide, the mass is suspended in a dilute solution of HCl as the positive pole, the negative pole consisting of a rod of carbon connected with a battery of two or three cells. The combined action of the acid and current dissolves away the metal, the silicide remaining intact. The crystals of silicide fall to the bottom of the vessel as they are liberated. These are treated first with aqua regia and then with ammonia, to remove the last traces of tungsten, and pure Si_3W_2 is left, which is crystalline, in the form of metallic-looking plates. It is heavy, having a density of 10·9; it is attacked by chlorine, bromine, and iodine at temperatures of about 300—500°; it burns brilliantly in pure oxygen at about 500°. Hydrochloric and nitric acids have no action in the cold; also the action of aqua regia is inappreciable; but a mixture of nitric and hydrofluoric attacks it violently. Silicide of tungsten is analysed in the following manner:—The silicide, contained in a glass vessel, is decomposed by chlorine at a high temperature; chlorides of tungsten and silicon are formed. The silicon chloride, being more volatile, is separated, converted into silica, and weighed. The metallic chloride is treated with nitric acid, forming tungstic acid, which is calcined and weighed.

The Solubility in Water of Tricalcic Phosphate and of Apatite.—Jules Joffre.—The solubility of tricalcic phosphate in water is a question of great interest to chemists and others engaged in agriculture; for, however slight this solubility may be, it is of great importance in vegetable physiology. The author placed the phosphate in water for about two months, then filtered, and, after evaporation, the phosphoric acid was estimated as phospho-molybdate of ammonia. There is good reason to believe that two months is a long enough time for contact with water; for, after a submergence of several years, the author found analogous figures. The coefficient of solubility is found to be 0·009 grm. per litre. As carbonic acid is always present in the soil, the author made further experiments with water saturated with carbonic acid at the normal temperature, and found that the coefficient of solubility was 0·153 grm. per litre. He next made similar experiments with apatite, both in pure water and in water charged with carbonic acid. In pure water there was only 0·002 grm. per litre dissolved, and in water saturated with carbonic acid 0·014 grm. per litre.—*Bulletin de la Société Chimique de Paris*, Series 3, vol. xix.-xx., No. 9.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—Herbert William Allingham, F.R.C.S.; Mr. T. Newbold Piddocke: Mr. Edwd. Preedy; Mr. William Munro Tapp, LL.D.; The Hon. William Frederick Cuthbert Vernon; Mrs. Adela Wetzlar, and Dr. Charles Theodore Williams, F.R.C.P. The special thanks of the Members were returned to Dr. George Wyld, for his present of a portrait of Dr. Thomas Garnett, first Professor in the Royal Institution.

City and Guilds of London Institute.—The following Scholarships have been awarded in connection with the present Session, 1898-99, of this College:—Clothworkers' Scholarship, £60 a year, to A. J. Cook; Mitchell Scholarship, £50 a year, to R. H. Collins; John Samuel Scholarship, £30 and free education, to F. C. Hounsfield; Institute's Free-Studentships, to R. H. Buckie, A. W. Harrold, and W. H. P. Brounger.

A Catalogue of Scientific Books and Periodicals.—We have received the first number of a new publication entitled *Bibliographie des Sciences et de l'Industrie*, which will be published on the 5th of each month, and sent free of cost to anyone who applies for it. The object of the publication is to give in a concise form a summary of all the new books and periodicals bearing on scientific subjects, viz., electricity, chemistry, architecture, geology, mathematics, and legislation, both administrative, industrial, and commercial. The prices of all these publications are given, and any of them will be sent on receipt of a postal order or cheque. This catalogue is issued by Vve. Ch. Dunod, 49, Quai des Grands-Augustins, Paris.

Estimation of Tannin.—Léo Vignon.—A new method of estimating tannin is based on the following principle:—Given an aqueous solution of tannin, this substance, to the exclusion of other bodies which generally accompany it (gallic acid, glucose, &c.), is absorbed readily and almost in entirety by undressed silk; it is sufficient to keep the silk-tannin mixture dissolved from four to five hours at 50° C. and to use the silk in large excess of the tannin. The tannin thus absorbed may be estimated by several methods, of which the most exact is described at length.—*Comptes Rendus*, cxxvii., No. 8.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Queries.—(1) What are the estimated specific gravities of liquid oxygen and of liquid hydrogen. (2) What is the crystalline form of the element manganese, and where would one find a thorough treatment of the physical properties of the element manganese?—W. L. T. Addison, Byng Inlet, Ontario, Canada, Nov. 16, 1898.

MEETINGS FOR THE WEEK.

Monday, 12th.—Society of Arts, 8, (Cantor Lectures). "Acetylene," by Prof. Vivian B. Lewes.

Wednesday, 14th.—Society of Arts, 8. "Commercial Education," by Sir Albert Rollit, M.P.

Thursday, 15th.—Chemical, 8. "Interaction of Ethylic Sodiomalonate and Mesityl Oxide," by A. W. Crossley, Ph.D. "Derivatives of Camphoric Acid. Part III.," by F. S. Kipping, D.Sc., F.R.S. "Synthesis of $\alpha\beta\beta$-Trimethylglutaric Acid," by W. H. Perkin, jun., F.R.S., and J. F. Thorpe, Ph.D.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2038.

PREDICTIONS OF NEON.

By Lieut.-Colonel W. SEDGWICK, late R.E.

In Lord Lister's Address at the Anniversary Meeting of the Royal Society on November 30th, 1898, reference was made to the fact that there were grounds for anticipating the existence of a non-valent element of the atomic weight of neon.

In the Chemical News, vol. lxxi., pp. 139—140, I showed that the metalloid series—

$$F^{II}., 19; O^{II}., 16; N^{III}., 14; C^{IV}., 12$$

pointed strongly to the existence of a non-valent element of atomic weight 20; and that one of the metal series also pointed just as strongly to the same fact; and thus that both of these series had been derived from a non-valent element of atomic weight 20. The metal series in question was, of course—

$$Na^{I}., 23; Mg^{II}., 24; Al^{III}., 27.$$

But I further showed that, in "Force as an Entity," published in 1890, I had (at p. 61) previously pointed out in effect that the above metalloid series showed the probable existence of a non-valent element of atomic weight 20; and (in a paper submitted to the officers of the Royal Society on November 16th, 1892) that the metalloid and metal series both showed the same fact. I may add that in that paper, which was on "The Form of the Atom," I showed a non-valent element of atomic weight 20—21 as "assumed to exist," bringing forward both the metal and the metalloid series shown above to support the assumption, and pointing out the probability that both of these series had a common origin in a non-valent element of that atomic weight.

On each of these occasions my object in pointing out the probable existence of this and several other non-valent elements was to show that with these non-valent elements it was possible to deduce the form of the atom, both for metals and metalloids; the form obtained being, for non-valent atoms a perfect sphere, and for valent atoms a sphere with flat places in number corresponding with valency—the monovalent having one, the divalent two, and so on. In the metalloid atom the flat places are cut down, so that atomic weight decreases as valency increases; and in the metal atom they are built up, so that atomic weight increases as valency increases; and, accordingly, the same non-valent element can give rise both to a metalloid and a metal series.

Professor Julius Thomsen in *Zeit. für Anorg. Chemie*, vol. ix., p. 283, refers to my paper in the Chemical News, vol. lxxi., p. 139, in giving his conclusions in regard to the origin of the elements based on their electrical behaviour. He obtains a diagram which manifestly finds a perfect and complete physical expression in the form for the atom obtained from valency as shown above.

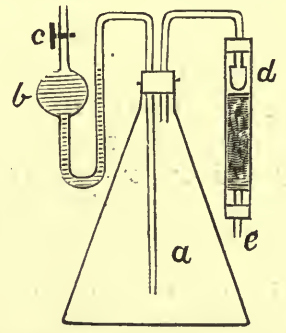
In regard to Clerk-Maxwell's objection that the hard atom "fails to account for the vibrations of the molecule as shown in the spectroscope" (Art. "Atom," "Ency. Brit.," 9th ed.), it may be pointed out that, with an ether composed of two fluids, it is not necessary to refer the disturbance which gives rise to light to any vibratory movement in the atom. Our ocean waves and ocean breakers are not due to any vibratory movement in our earth, but are due to the presence of two fluids. And we may remember that Newton said in effect that he would accept the undulatory theory of light if he could see his way to getting an ether composed of two fluids ("Opticks," 3rd ed., p. 339).

December 12, 1898.

A SIMPLE APPARATUS FOR THE ESTIMATION OF CARBON DIOXIDE.

By W. H. BARKER, B.Sc., F.C.S.

The construction of this apparatus can easily be understood from the figure. It consists of a conical-shaped flat-bottomed flask, fitted with a cork having two holes. Through one of these holes is inserted a bent glass tube, the drawn-out end of which nearly touches the bottom of the flask; near the other extremity of it a bulb, *b*, is blown, in which the acid is placed. The tube may be opened or closed by means of a short piece of rubber tubing provided with the clip *c*. Through the other hole of the cork is inserted a bent glass tube connected with a straight $CaCl_2$ tube, in the upper part of which is placed the closed end of a test-tube, *d*, about an inch long, the



rest of the tube being filled with $CaCl_2$. This arrangement prevents the $CaCl_2$ from becoming unnecessarily moist.

In carrying out an analysis, after the carbonate has been placed in the flask and the necessary weighings made, a rubber tube is attached to *e* and the clip *c* opened. By suction through the rubber tube a small quantity of acid is drawn into the flask and the clip is quickly closed. The bent tube with the bulb containing the acid now acts as a syphon, and therefore, by means of the clip, the flow of acid into the flask can be regulated. The analysis is completed by warming the flask and aspirating air through the apparatus by suction through the rubber tube, which is removed before the final weighing is made.

NOTE ON THE DESTRUCTION OF SOAP BY WATER.

The Soap Test and Lime Water.

By ROBERT MELDRUM, F.C.S.

The following experiment as regards the destruction of soap by hard water, though not so accurate as it ought to have been, is nevertheless interesting, as the number of such determinations pubished is not very numerous.

The water experimented with had a total hardness of 38° per gallon,—permanent 22°, temporary 16°,—and was fairly constant. A pint of the water was taken, to which was added 1 grm. of the soap (primrose) dissolved in a little of the water and well shaken. The lather produced disappeared completely in a minute, but on re-shaking appeared, but was not permanent. Another grm. of the

soap, dissolved in 25 c.c. of the pint, was added, and on agitating a lather resulted, and had every appearance of being permanent. The mixture of magnesia and lime soaps was filtered on to a tared filter, washed with distilled water, and dried at 100° C.

Paper + insoluble soaps = 1·879 − 0·803 = 1·076 grms. CaO in soaps = 0·086 grm. = 7·99 per cent. Assuming that 100 parts anhydrous insoluble soaps = 130 ordinary soap, then soap destroyed per pint = 1·398 grms. = 21·5 grains = 172 grains per gallon = 24·5 pounds per 1000 gallons. As this water is actually in use on an industrial scale, 1000 gallons at least being used daily, it will be seen that the loss of soap per week through this cause must be considerable. It is not unusual to find waters of this degree of hardness being used on the large scale for washing operations.

Carbonate of lime, in suspension, causes hardness just as well as if in the soluble state. A cloudy suspension of $CaCO_3$ in CO_2 free water gave a hardness of 6° per 100,000. On adding a little more $CaCO_3$ the latter disappeared.

CO_2 by itself also causes hardness. Thus 10 c.c. saturated CO_2 added to 40 c.c. distilled water (free CO_2) required 6 c.c. for permanent lather. These lathers are always very feeble.

Soap solution is not a reliable standard for determining the amount of CaO present in very weak lime water, as will be seen from the following.

Grains per gallon of CaO in distilled H_2O :—

13·4, 13·4, 6·7, 6·7, 3·3, 3·3, 3·3.

C.c. soap required to lather 70 c.c. of above :—

17·0, 17·5, 13·0, 13·0, 12·0, 12·5, 9·5.

It is remarkable that these lathers only persist for two or three seconds, whereas natural waters as rich as these in lime will, generally, give permanent lathers. In all cases where the lather does not persist, or is very weak, it is a good plan to add a little NH_4Cl, which has usually the effect of making the otherwise feeble lather strong. I have never found this to interfere with the accuracy of the test, and have always found it to be of the greatest advantage.

BLANK TESTS.

So long as "blind tests" or "blanks" are necessary evils, it is important that they should actually indicate the correction which must be applied to analytical results to account for impure reagents.

It would seem that so apparently simple a matter could be settled off hand once and for all; but when the element to be estimated exists only in hundredths of 1 per cent—less in amount mayhap than is introduced by the reagents, then the method of determining the blank is of some moment.

Take the estimation of sulphur in steel, for instance, by the aqua regia and barium sulphate process. It is well known that the purest acids obtainable are never perfectly free from sulphur, and equally well known that an error of from 0·005 to 0·01 per cent would considerably enhance or deteriorate the value of high class bar-iron.

Arnold ("Steel Works Analysis," p. 99) advises that the usual volume of acids should be passed through the ordinary operations—which includes baking on the hottest part of the plate for at least half an hour—with a pinch of Swedish bar-iron "to fix the sulphuric acid as non-volatile sulphate of iron." Blair ("Chem. Anal. of Iron," p. 65) makes no mention of the "blank," but remarks that in the actual analysis "Carbonate of sodium is to be added to prevent any possible loss of sulphuric acid, which might otherwise occur by the decomposition of the sulphate of iron at a high temperature." N. W. Lord ("Notes on Metallurgical Analysis," p. 51) justifies the same procedure with still greater emphasis—"as the sulphates of iron are easily decomposed by heat."

Generally descriptions of this process do not refer to the necessity for a "blank." It is very common, however, to proceed as Prof. Arnold does, but substituting a little soda carbonate for the Swedish bar-iron.

Without discussing the merits of the separate means of fixing the sulphuric acid, it may be pointed out that neither way is really satisfactory, because they do not even approximate to the conditions under which the barium sulphate is ordinarily obtained. Where the amount of sulphur in an iron is exceptionally low, and the blank unusually high, the subtraction of the blank obtained as above may leave a negative result.

The following procedure, which has been acted upon for eight or ten years, and of which no published account has yet been seen, is offered as affording a close approximation to empirical accuracy in the determination of this and similar blanks :—

Take two separate amounts of steel weighing A and 2A grms. respectively, and by the usual process obtain from each the sulphur as barium sulphate. Then—

$BaSO_4$ (A) = $BaSO_4$ in A grms. Fe + blank (1)

$BaSO_4$ (2A) = $BaSO_4$ in 2A grms. Fe + blank (2)

(1) × 2 = 2$BaSO_4$ (A) = $BaSO_4$ in 2A grms. Fe + 2 blanks (3)

(3) − (2) = $BaSO_4$ due to blank.

Thus obtained the blank is usually lower than that obtained by evaporating the same volume of acids with a little soda carbonate.

J. T.

THINOLITE.

By ARTHUR M. EDWARDS, M.D., F.L.S.

THINOLITE is a mineralogical "species," so-called; but what a species is exactly in this case it is difficult to understand; for I do not believe in species at all. Things can exist in forms which can be distinguished by sight one from the other; but what are "species," the different persons who view them differ themselves. In man, one man—the negro—is one species, and another divides the negro up into several species. So one calls thinolite a true species: another says it is a variety of Gaylussite. Mr. Clarence King, who named it, does not say why thinolite is a species, nor what a species is. But he named it from being formed on the shore of a lake, from the Greek name meaning a lake shore. It was a tuffaceous mineral, and he supposed it to come from Gaylussite, a mineral species. Gaylussite was named after the celebrated French chemist and philosopher, Nicolas Francois Gay-Lussac, and is a hydrous compound of carbonates of lime and soda. It occurs in crystals which are lengthened and prismatic. Their lustre is vitreous; the colour white, or yellowish white, and translucent. They have a composition of :—Carbonate of soda, 30·9; carbonate of lime, 33·8; and water, 30·3; and a specific gravity of 1·92 to 1·90. It has been produced artificially by mixing eight parts by volume of a saturated solution of carbonate of soda with one of a solution of chloride of calcium. It is well to remember this fact, as it bears directly on what I have to say anent thinolite. Perhaps thinolite is Gaylussite after all. It was named by the celebrated Professor James D. Dana. His son, Professor E. S. Dana, examined specimens for the U.S. Geological Survey, and stated that Gaylussite was confined to the name of one kind of the tuffaceous mineral found by King. So thinolite is a "variety" of the "species" Gaylussite. But why he distinguished thinolite as a species, unless it is crystalline—and Gaylussite is crystalline also, and the composition is the same likewise—I do not see. It is chemically the same as the other tuffas, and is included in the species which King refers to. But let that pass,

The possession of a specimen which was gathered for Bacillaria—or diatoms as they were called—at Salt Lake Desert, Utah, and for which I have to thank the Hon. A. A. Adee, of Washington, D.C., who got it from the Smithsonian Institution, contains that mineralogical curiosity—thinolite. And this warrants me in saying something on the subject of the Salt Lake Desert; for it is part of the Occidental Sea, as we will see. Besides, I have it from the Yellowstone Park, where it is recent and forming now. Miss Josephine E. Tilden, of the University of Minnesota, sent me the specimen; and I hope to have still more, for she went to that region again in the summer of 1898. And these gatherings, along with others which I have, confirm me in my theory of the Occidental Sea, of which I wish to speak now.

In 1878 King founded thinolite. The name Lake Lahontan was given by him to a great lake, the remains of which he found there. He supposed it to have been a lake in Quaternary times—at least it was a lake in that time, although it had existed long before, in the Eocene, before the Neocene. How far back the Eocene was is, of course, undetermined. It was in Nevada, and the remains exist now as Pyramid, Winemucca, Carçon, and Humboldt Lakes; these are salt lakes—the remains of Lake Lahontan. The region was covered with fresh water before the Glacial Period, which is the later part of the Pleistocene Period. It was a large lake or sea, which I call the Occidental Sea in the Eocene Period. It broke through the elevated edge of the basin by becoming larger in water, or by the elevation of the bottom. The Sierra Nevada was elevated later, and formed the Columbia and Colorado rivers flowing to the north and south; the Sacramento and San Juaquin rivers, which are in California, flowing north and south also, were formed then; and perhaps the upper Missouri river. The water was fresh, as is shown by the Bacillaria left there, and became more and more brackish until it resulted in the very salt lakes—more salt than the ocean. But it must be remembered and understood that this was in ancient times—Eocene or earlier periods. As the sea evaporated, the water remained fresh until it was frozen over in the earlier Glacial Period. The earth was thin there, for volcanic fires melted it underneath, and it sunk by the weight of the ice there, and cracked, and fire came out, and formed the melted rock that is now there in parallel lines from north to south—the faulted monoclines of the great plains. But it did not return to its original state; that is to say, it did not go down again, but crowded up the Sierra Nevada on the west. The bottom was thus elevated, when the which was melted and poured out; and the ice was melted, partly by the heated rock; and the waters flowed off, as I have said, by the Columbia and Colorado rivers. In this way we can account for the different deposits of Gaylussite and diatomaceous earth which is found there and on the Columbia river; the river cutting through it in deep gorges, or cañons as they are called. As the water evaporated, it left, as I have said, Lakes Lahontan and Bonneville, which were brackish; and it continued to evaporate until it left the very salt lake called Pyramid and others in the west, and Great Salt and Sevier lakes in the west.

And the diatomaceous earth is siliceous, not silica at all, but a hydrate which is soluble in fresh and also in salt water; and is the solid material which is present as Gaylussite a "species," or thinolite a "variety."

Gaylussite or thinolite can be and is forming now in Yellowstone Park, and the Bacillaria which are living now are the descendants of the same Bacillaria which we find in the Neocene rocks of Monterey, California, and likewise in the diatomaceous earths of the Great Plain. We can also see them in the Neocene diatomaceous earths of the world, from Jutland, Denmark, to Oran, Africa, and from Atlantic City, New Jersey, to Tampa Bay, Florida.

The fresh-water Diatomaceæ are sources of silica very valuable in various uses besides the mere making of polishing powder, for which they are extensively quarried. But they are the Eocene rock which I years ago styled Sub-plutonic from the presence of volcanic tuffa there. And the Neocene Platonaceous rock has also come into use for various purposes.

VOLUMETRIC ESTIMATION OF VANADIUM IN PRESENCE OF SMALL AMOUNTS OF CHROMIUM,

WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.*

By W. F. HILLEBRAND.

Outline and Limitations of the Method.

When chromium and vanadium occur together, and the former has been estimated colorimetrically, as detailed in a previous paper (*Journ. American Chem. Soc.*, xx., 454; Chemical News, vol. lxxviii., p. 227), the vanadium can in many instances be at once estimated without separating from the chromium by the well-known method of titration with potassium permanganate in sulphuric acid solution after reduction by sulphurous acid and expulsion of all excess of the latter.

The application of the method is subject to one limitation—the chromium must not be present above a certain moderate amount. This limitation is due to the considerable amount of permanganate required to produce a clear transition tint when titrating in a hot solution, as is necessary with vanadium. In a cold solution of chromic sulphate much less permanganate is needed to produce the peculiar blackish tint without a shade of green, which affords a sure indication of excess of permanganate, but in a hot and especially a boiling solution the oxidation of the chromium (Storer, through "Gmelin-Kraut," ii., [2], 290) itself takes place so rapidly that a very large excess of the reagent may be added before a pronounced end-reaction is obtained. Nevertheless, as will be shown, quite satisfactory determinations of as little as 1 or 2 m.grms. of vanadium pentoxide can be made in presence of as much as 30 m.grms. of chromic oxide.

Inasmuch as chromium is almost never a prominent constituent of the clays, coals, iron ores, and rocks in which vanadium has been thus far reported, the method promises to be of great advantage in rock and ore analysis, where these elements probably frequently occur together, generally with phosphorus and sometimes arsenic. It is not directly applicable in presence of molybdenum, and arsenic must first be removed by hydrogen sulphide if present.

Testing the Method.

A solution of sodium vanadate was prepared by fusing 0·937 grm. of pure vanadium pentoxide with sodium carbonate and diluting to 1 litre. Each c.c. contained 0·000937 grm. vanadium pentoxide. Of this, sufficient amounts were mixed with varying volumes of a standard solution of potassium chromate. After in some cases determining chromium colorimetrically, sulphuric acid was added, sulphur dioxide gas† introduced for a few moments, and the excess of the latter expelled by boiling in a rapid current of carbon dioxide, without which its complete expulsion is difficult. When cooled to from 70—80° C., the titration was made with very dilute solution of permanganate corresponding to about 1 m.grm. vanadium pentoxide to the c.c. as calculated from its

* Read before the Washington Section, April 14, 1898. From the *Journal of the American Chemical Society*, xx., No 6, June, 1898.

† The direct use of a solution of sulphur dioxide or of an alkaline sulphite is inadmissible unless these have been freshly prepared, since after a lapse of time they contain other oxidisable bodies than sulphurous acid or a sulphite. The sulphur dioxide is best obtained as wanted by heating a flask containing a solution of sulphur dioxide, or of a sulphite to which sulphuric acid has been added.

TABLE I.

No.	Chromic oxide. M.grms.	Vanadium pentoxide. M.grms.	Vanadium pentoxide found. M.grms.	Error. M·grm.
1.	1	9·37	9·22	−0·15
2.	1	0·94	1·04	+0·10
			0·98	+0·04
3.	1·5	5·25	5·49	+0·24
			5·43	+0·19
4.	2	5·62	5·5	−0·12
			5·5	−0·12
5.	3	4·68	4·78	+0·10
			4·78	+0·10
			4·83	+0·15
6.	3	5·62	5·58	−0·04
			5·58	−0·04
7.	3·5	18·74	18 89	+0·15
			18·97	+0·23
8.	6	5·6	6·1	+0·50
9.	6	4·68	4·78	+0·10
10.	6	5·62	5·58	−0·04
11.	10	5·62	5·58	−0·04
12.	10	23·52	23·81	+0·29
			23·71	+0·19
13.	10	46·85	46·98	+0·13
			47·20	+0·35
14.	25	23·52	23·65	+0·13
			23·75	+0·23
15.	87·5	23·52	23·71	+0·19

TABLE II.

Showing application of Degree of Correction for Larger Amounts of Chromium, obtained by adding Potassium Permanganate to an Equal Bulk of Solution containing a like amount of Chromic Sulphate.

No.	Chromic oxide. M.grms.	Vanadium pentoxide. M.grms.	Vanadium pentoxide. found. Uncorr.	Vanadium pentoxide. found. Corrected.	Error. M.grm.	Volume of solution.
16.	20	0·94	1·59	0 99	+0·05	50—100 c.c.
17.	20	1·87	2·69	2·09	+0·22	,,
			2·39	1 79	−0·08	
			2·59	1·99	+0·12	
18.	20	18·74	19·4	18·73	−0·01	,,
			19·3	18·63	−0·11	
			19·3	18 63	−0·11	
19.	30	1·87	2·99	2·14	+0·27	About 100 c.c.
			2·79	1·94	+0·07	
			2·79	1·94	+0·07	
			2·69	1·84	−0·03	
			2 69	1·84	−0·03	
20.	30	1·87	2·69	1·79	−0·08	200 c.c.
			2·89	2·09	+0·22	
			2·89	2·09	+0·22	
			2·79	1·89	+0·12	
21.	62	46·85	48·60	47·60	+0·75	200 c.c.

TABLE III.

No.	Chromic oxide. M.grms.	Vanadium pentoxide. M.grms.	Vanadium pentoxide found. M.grms.	Vanadium pentoxide. Error. M.grm.
22. (Five grms. iron ore)	7	6·76	6 81	+0·05
			6·48	−0·28
			6·43	−0·33
			6·37	−0·37
23. (Five grms. iron ore)	3	3	3·08	+0·08
			3·13	+0·13
			3·03	+0·03
			3·08	+0·08
24. (Two grms. silicate)	1·6	1·87	1·86	−0·01
			1·97	+0·10
			2·07	+0·20
			1·86	−0·01

equivalent in iron. By repeating the reduction and boiling, any number of check tests can be rapidly made in the same solution. The solutions ranged in bulk from 50 to 200 c.c., according to the amounts of chromium added.

With the larger chromium contents the differences in the quantity of permanganate used, according as titration was effected at practically boiling temperature or a somewhat reduced one, were very apparent. In one case, at nearly boiling heat, 10 m.grms. of chromic oxide were largely oxidised to chromium trioxide, as shown by the change of colour from dark green to yellow. Even at 70—80° with this amount of chromium the results for vanadium will be too high unless the precaution is taken to ascertain the needed correction by adding permanganate to an equal bulk of hot chromic sulphate solution containing approximately the same amount of chromium. When this is done, however, the results are satisfactory even when as much as 30 m.grms. of chromic oxide are present and only 1 or 2 m.grms. of vanadium pentoxide.

Doubtless the modified iodometric method of T. Fischer ("Inaugural Dissertation," Rostock, 1894, p. 33) will in general give sharper results where chromium is present in considerable amount, and if so it should be preferred to titration by permanganate. But its use involves the preparation of a standard thiosulphate instead of the ever ready permanganate solution, and the manipulations are more time-consuming. The object has been in the present case to reach satisfactory results with the greatest expedition, and when chromium is not present in considerable amounts this is accomplished.

The accompanying tables contain the results of a considerable number of tests, those in Table II. being tabulated separately in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction above mentioned, and also the amount of this correction.

In spite of the fact that the correction in most of the trials of this last table represents a large proportion of the permanganate used, the results must be considered satisfactory in view of the small amount of vanadium present, and they show that the method in competent hands after a little experience affords trustworthy figures.

Testing the Method on Rocks and Ores.

The following table shows its availability for rocks and ores. Known amounts of both chromium and vanadium were added to an iron ore and to a silicate, both free from arsenic, which were then fused with sodium carbonate and nitrate and further treated as follows:—After extracting with water and reducing manganese by alcohol, the silica and alumina were mostly removed by nearly neutralising with nitric acid and evaporating to near dryness. The washed precipitate was ignited and treated with hydrofluoric and sulphuric acids, the residue fused with sodium carbonate, since it frequently contains a little chromium, and again nearly neutralised, &c. To the combined and slightly alkaline filtrates was added mercurous nitrate, the precipitate of phosphate, vanadate, chromate, and carbonate was ignited in platinum, fused with a little sodium carbonate, leached with water, and filtered into a small graduated flask. After colorimetric determination of the chromium, sulphuric acid was added; both chromium and vanadium were reduced by sulphur dioxide gas, and the titration carried out as described.

These and other experiments show that, by taking not over 5 grms. of ore or rock, vanadium, if present to the extent of 0·01 or 0·02 per cent, can be readily estimated by exercising reasonable care in all the operations. Absolute confirmation of its presence can be easily obtained by evaporating and igniting the solution to remove excess of sulphuric acid, taking up with a few drops of dilute nitric acid, and adding to the solution in a test-tube a drop or two of hydrogen peroxide. In this way positive or negative assurance as to the presence of vanadium is given when the result of titration alone might be uncertain. Addition of ether at the same time affords a

simultaneous test for chromium by its blue colour, and this might perhaps be made use of, if necessary, to remove all or the greater part of the chromium prior to titration of the vanadium, since the oxidation product of the latter does not dissolve in the ether.

It is even possible that the dark brown colour produced by hydrogen peroxide might be utilised for an exact colorimetric method for estimating vanadium.

THE SOLUTION OF SOLIDS AND LIQUIDS IN GASES.

By P. VILLARD.

THE phenomenon of the solution of a solid in a liquid—of a metallic salt in water, for example—consists of a change of state, of a veritable fusion in fact, by which the solid is enabled to become intimately mixed with the solvent liquid. There is nothing to prevent us generalising this notion, and admitting that every fluid, gas as well as liquid, can by its action on solid or liquid bodies which may be plunged therein, bring this body to a physical state in which they will become mixed, or in a word dissolved to a greater or less degree. Such a supposition is the more acceptable as the possibility of passing without transition from the solid to the gaseous condition has been proved long ago.

Experiment shows that gas possesses, with regard to both solids and liquids of little volatility, a dissolving power sometimes very considerable. If this power is not generally recognised under ordinary conditions, it is only due to the slight density of the gas compared with that of even the lightest liquids.

The first experiments relating to this question gave very distinct results. In 1880 Messrs. Hannay and Hogarth observed the solution of bromide of potassium, iodide of potassium, and chloride of iron, dissolve in the vapour of alcohol heated to +375° under pressure,—that is to say, at a temperature at which alcohol can only exist in the state of vapour, for it is then above its critical point. The same year M. Cailletet dissolved liquid carbonic anhydride in compressed air.

These first results give a valuable indication, showing that the power of dissolving does not belong exclusively to liquids. Without even speaking of its possible applications, there is a theoretical interest to be found in studying the phenomena of solution under such novel conditions, and with solvents whose constitution is more simple than that of liquids.

The experiments we have just referred to were made either at a high temperature or by using, as the body to be dissolved, a gas liquefied by pressure,—that is to say, a liquid of extreme volatility. These are not the only experiments which have been made in this direction; but no one appears to have tried whether, at the ordinary temperature, gases possess the property of dissolving bodies which are under ordinary conditions solid or liquid. Such a property, however, exists, and it is easily shown; it suffices to use compressed gas; the pressure, further, only appears to have an indirect influence on the phenomenon, viz., in increasing the density of the fluid.

I here give the results obtained at about +17°, except when otherwise stated, with gases for the most part permanent at this temperature.

I. *Oxygen, Air, Hydrogen.*

It is easy to watch the solution in oxygen of a liquid such as bromine, the vapour of which is coloured. It suffices to place a drop of bromine at the bottom of a narrow glass tube, and to pass in oxygen by the upper end; the oxygen must be compressed to about 200 atmospheres. The bromine vapour is first of all dispersed, but collects again near the liquid, but at the same time the colour becomes much more intense; diffusion then gradually takes place, and the colouration eventually fills the whole interior of the tube, the atmospheric contents of which presents a much deeper tint than before the compression.

The same result is obtained more rapidly by slanting the tube until it is almost horizontal; the gaseous layer, rendered more dense by its admixture with the vapour of bromine, spreads out and then diffuses all along the tube, to be replaced by still pure oxygen, on contact with which the liquid gives off more vapour, and in a very short while the colouration of the gas becomes uniform. The intervention of compressed oxygen has had the effect of turning a notable quantity of bromine into gas, which is added to the vapour already present in the apparatus, and of considerably increasing its density. This action is comparable with that exercised by a liquid on bodies which it dissolves—it is, in fact, a phenomenon of solution. When the pressure is diminished (the variation of pressure should be slow, so as not to sensibly affect the temperature), the colour becomes fainter, and at the same time small drops of bromine are deposited on the surface of the tube; thus we get the opposite of the previous experiment. These drops disappear again if the pressure is increased, and the colour of the gas becomes as deep as before. The solution of a very appreciable amount of bromine in compressed oxygen is thus made quite manifest.

Towards 300 atmospheres the colouration obtained far exceeds that of bromine water; it is practically the same as with six or seven times the thickness of ordinary saturated vapour of bromine,

It is, however, not necessary to have recourse to such great pressures to observe the phenomenon. The effect produced by oxygen is noticeable after a pressure of 4 atmospheres is reached, and is very marked at from 50 to 100 atmospheres. Under this last pressure the density of the dissolved bromine appears to be about three times the density of saturated bromine vapour *in vacuo*.

Air behaves in a very similar manner to oxygen; however, everything else being the same, the colouration obtained is a little fainter.

Iodine is also dissolved in oxygen in sensible quantities, but the phenomenon is not easily seen until the pressure is over 100 atmospheres and in tubes of at least 5 m.m. in diameter.

Hydrogen, which is both the lightest gas known and one of the most difficult to liquefy, only possesses a very feeble dissolving power; it can, however, be observed with bromine at pressures of 200 to 300 atmospheres.

II. *Formene.*

Formene is a very convenient body for dissolving notable quantities of liquids such as chloride of ethyl, sulphide of carbon, alcohol, or solids like camphor or paraffin. With this solvent it is not necessary to use very great pressures to show that the solubility of a liquid or of a solid in a gas may be as great as when using a liquid solvent. Thus chloride of ethyl dissolves in five or six times its volume of formene compressed to 180 atmospheres; at 200 atmospheres, at about 17°, the quantity of chloride that can be dissolved is such that the two fluids become miscible in any proportion, and the surface of separation between the liquid and the gas disappears. The same phenomenon is produced with sulphide of carbon towards 550 atmospheres at the ordinary temperature and at only 250 atmospheres at +150°.

Iodine is easily soluble in formene, to which it gives a lovely violet colour, which is very intense at 300 atmospheres even when examined through a thickness of only 2 m.m. We can also dissolve camphor and paraffin, and that in very noticeable quantities even with only ½ a c.c. of compressed formene,—that is to say, less than a decigrm. On removing the pressure these bodies are deposited; the iodine and camphor crystallise on the surface of the tube, paraffin gives rise to a more or less abundant crop of brilliant flakes throughout the tube.

III. *Ethylene.*

Iodine dissolves in ethylene in sufficient quantity to colour it a very deep violet through a thickness of 2 m.m., at about 300 atmospheres. If this solution is allowed to stand for an hour or two it loses its colour, on account of the combination of the iodine with the ethylene; the iodide of ethylene formed remains in solution; when the pressure is released it is deposited in crystals, which are again dissolved if the pressure is re-established. Above 150 atmospheres ethylene dissolves paraffin abundantly; on removing the pressure the latter resumes the solid state, and forms a kind of felted mass throughout the tube.

Ordinary stearic acid is also dissolved, but in much less quantity than paraffin.

Camphor gives rise to a special phenomenon: if the pressure is moderated it immediately assumes the gaseous state, as with formene; if, on the contrary, the pressure reaches 150 atmospheres, the undissolved camphor becomes liquid, and then dissolves in the gas when this pressure is exceeded. The same phenomena take place in the inverse order as the pressure is released: there is first deposited a liquid formed of camphor and ethylene; at 150 atmospheres this liquid becomes solid; the camphor deposited below this pressure takes the solid state without transition.

IV. *Protoxide of Nitrogen, Carbonic Acid.*

Bromine dissolves in protoxide of nitrogen at 20 atmospheres, in the same manner in which it dissolves in oxygen at about 40 atmospheres. Compressed carbonic acid sensibly dissolves iodine, taking a violet colour. The dissolving power of these gases which can be liquefied at the ordinary temperature does not appear to be in any way extraordinary. But the pressures which can be obtained are limited by the liquefaction of the gas, at least if we do not exceed the critical temperature.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE BANQUET TO PAST PRESIDENTS.

Professor Dewar, F.R.S., President, in the Chair.

(Concluded from p. 289).

"The Foreign Members."

Sir William Crookes—"If it is possible for an after-dinner speaker to associate the word pleasure with the duty he has to perform, then I may lay claim to a slight feeling of that kind; for we are here assembled to do honour to our Past-Presidents, who are, as it were, now celebrating their jubilee in the Chemical Society. But it so happens that I also have a little jubilee of my own at this time, for exactly fifty years ago I made my first step in science by entering the Royal College of Chemistry. I remember as if it were yesterday, on a dull November morning, being introduced to Hofmann, who forthwith installed me at a bench, and asked Spiller, who was a few weeks my senior in science, to put me through the gases, preliminary to a course of the 'Giessen Outlines.' These were the days of compound ammonias, and heating in sealed glass tubes under pressure: having a certain facility at the blowpipe, I used to seal up some of these tubes; many of them, I fear, burst, for I well remember Hofmann's quaint remark, while watching one of them with anxious eyes, 'I think, Mr. Crookes, it will now gradually commence to explode violently.'

"One of the great troubles of a long life is to see the friends of early days drop off one by one. Of those in the College when I entered, I know only of Abel, Buckton, Dent, Spiller, and one or two others. It is a special pleasure for me to be here to-night and join in doing honour to one of these—my oldest scientific friend—Sir Frederick Abel. But in these reminiscences I must not forget my duty. I am asked to propose the health of the Foreign Members of the Society. There is a little topsyturveydom about this arrangement. I am saddled with a burden to which I have only a doubtful right. Such a toast can only be proposed by a Fellow, but when, some time ago, I approached your senior Secretary in that capacity, he refused to regard me in this light, and said I could only dine among you as a visitor.

"But the occasion is so special that, as a visitor, outsider, or Fellow, it must always be a great pleasure to propose the toast of the Foreign Members. We have a large roll of Foreign Members on our list. They are very eminent men; and, as proof, I need only mention that on this special occasion they are so busy with scientific work that few are able to come to join us to-night. But we have amongst us one of the most eminent of Continental chemists—Professor Ostwald—whose name is a household word to us all, and I will ask him to take the burden of replying to this toast."

Professor Ostwald—"The task laid upon my shoulders is so heavy that I cannot bear it in a foreign language. I must ask you, therefore, to allow me to answer in my own. Als ich die ehrenvolle Einladung für den heutigen Tag erhielt, war ich sofort bereit zu kommen. Nicht weil ich eine grosse Zahl guter Freunde und werthvoller Dinge in London sehen konnte; ich kam um eine grössere Sache. Ich kam, um Zeugniss abzulegen von der Gemeinschaft der wissenschaftlichen Männer aller Nationen. Das Fest, welches Sie feiern, hat seinen Anklang in der ganzen Welt gefunden; die wissenschaftliche Internationalität bringt es mit sich, dass des heutigen Tages überall gedacht wird, wo Chemiker sind.

"Meine Herren! Die Wissenschaft ist ein Land, welches die Eigenschaft hat, um so mehr Menschen beherbergen zu können, je mehr Bewohner sich darin sammeln; sie ist ein Schatz, der um so grösser wird, je mehr man ihn theilt. Darum kann jeder von uns in seiner Art seine Arbeit thun, und die Gemeinsamkeit bedeutet nicht Gleichförmigkeit. Wir werden immer an unseren französischen Arbeitsgenossen die Klarheit ihrer Darstellung und die Strenge ihrer logischen Entwickelung bewundern. Die Originalität der Gedanken und die unwiderstehliche Energie ihrer Durchführung wird stets die englische Forschung auszeichnen, und wenn wir Deutsche 'durch die Welt mit allen Sinnen schweifen,' um für unsere Arbeit eine möglichst breite Unterlage und einen möglichst weiten Horizont zu gewinnen, so thun wir darin auch nur, was unserer Natur entspricht.

"Hierzu möchte ich aus unserer Wissenschaft ein Beispiel entwickeln. Es ist ein wichtiges Resultat der heutigen Forschung, dass es nicht möglich ist, einen absolut reinen Stoff herzustellen. So rein er auch wird: die letzten Spuren seiner Mutterlauge können nicht entfernt werden, und er trägt immer ein Zeugniss seiner letzten Geschichte mit sich.

"Nun, meine Herren, in der Chemie des Geistes gilt ein ähnliches Gesetz. Auch der klarste Gedanke, die durchgearbeitetste Theorie trägt Spuren der Umgebung mit sich, aus der sie entstanden ist. Wenn nun der Fremde den neuen Gedanken zum ersten Male zu Gesicht bekommt, und er gefällt ihm nicht, so wird er sich zunachst nicht bewusst sein, ob der abstassende Eindruck von dem Gedanken selbst, oder von der anhängenden Mutterlauge herrührt, und es kann kommen, dass er ihn verwirft, nicht wegen seiner eigenen Beschaffenheit, sondern wegen zafälliger Beimengungen. Wenn ihm aber jenes *Gesetz der geistigen Mutterlauge* bekannt ist, so wird er sorgfältiger prüfen, und manches Vorurtheil, welches die gameinsame Arbeit der Nationen stört, wird fallen.

"Für diese Gemeinsamkeit bietet gerade der heutige

Abend einen ausgezeichneten Beleg. Als ich die Geschichte meines besonderen Gebietes, der Verwandtschaftslehre studirte, fand ich aus sehr früher Zeit eine Reine hochwichtiger Arbeiten, durch welche eine Anzahl fundamentaler Thatsachen festgestellt wurden. Die Arbeiten trugen den Namen des Dr. Gladstone. Ich habe vergeblich darauf gewartet, dass heute Abend diese Arbeiten erwähnt würden. Es ist nicht geschehen, und ich glaube, Dr. Gladstone hat selbst, vergessen, dass er sie gemacht hat. Aber wenn er sie auch selbst vergessen hat, die Wissenschaft wird sie nie vergessen. Und wenn jetst nach soviel Jähren, die Wissenschaft in Schweden, Holland, und Deutschland den Faden dort weitergesponnen hat, wo Dr. Gladstone in England ihn aus der Hand gelegt hat, so haben Sie ein schlagendes Beispiel vor sich, wieweit über Raum und Zeit die wissenschaftliche Gemeinsamkeit aller Forscher reicht."

"The Learned Societies."

Lord Reay—"I have seldom had the honour of proposing a toast to so distinguished an assembly, and at the same time a toast which, whether it was proposed at St. Petersburg, at Berlin, in Paris, in Vienna, or in Rome, coupled with the names with which it is coupled to-night, would attract the same applause. Lord Lister has conferred on the House of Lords, in entering it, an additional dignity. If we are asked—and we are occasionally asked—why there is a House of Lords, I do not know that we can give any better answer than by saying that the House of Lords is the proper place for receiving the princes of science. And, gentlemen, among the characteristics of the House of Lords there is one to which I shall allude,—one which I consider a very important characteristic. If I ask what are the characteristics of the House of Commons,—what are the characteristics of those who wish to enter the House of Commons,—then I am told that the catechism to which one has to answer is, 'Are you sound on Labour?' Now I am not quite sure that I fully grasp what is meant by soundness on Labour. But the problem may be solved when the House of Commons approaches a task which I know would tax the efforts of all the learned societies in London to deal with—the question of old age pensions. What is the catechism of the House of Lords? I think the question would be, 'Are you sound on Science?' I believe the House of Lords is sound on science, and in the contests of the future between prejudice and the laws of science, I think you will find, as you have found in the recent debate on vaccination, that the House of Lords will be on the side of Science, and not on the side of prejudice. And if the House of Lords is to remain sound on Science, then it will be due to having in its midst men like my noble friend Lord Lister, to keep it straight whenever it may show any inclination to diverge from the dictates of Science. There is hardly any subject at present in any department of the public service in which the question of science does not play a prominent part. And I do not believe that there is any department of the public service which does not occasionally seek the aid of a learned society on one or other of the scientific problems it has to solve. My late distinguished friend M. Léon Say used to predict of the twentieth century that Cabinets would be formed on the basis of sanitation. If so, we may still hope to see my noble friend Lord Lister at the head of the Home Office.

"With this toast is also coupled the name of my friend Professor Michael Foster. Mr. President and gentlemen, it is to me personally a great pleasure to couple with this toast that name, because the future of scientific education in London is committed to the care of Professor Michael Foster. The Statutory Commission, I hope, will set at rest that interminable controversy about the re-constitution of the University of London, and to Professor Michael Foster will fall the duty of settling the future of Science in that institution, which will influence the future of Science in our great empire. Let me conclude with an observation which is the result of what fell from the eloquent lips of the gentleman who last addressed us. He has spoken of 'die wissenschaftliche Internationalität.' I heard those words with great pleasure. Whatever causes of discord may disturb international relations, it will be among the great features of the work of the Learned Societies that they will always entertain cordial relations with the learned men in all foreign countries. And, Mr. President and gentlemen, whatever may happen on the banks of the Nile, of this I am sure, that the cordial relations which have existed between my distinguished friend Professor Ramsay on the banks of the Thames, and Monsieur Berthelot, on the banks of the Seine, will remain the same and tend to knit together that which ought never to be separated if the progress of civilisation is not to be interrupted. I give you the toast of 'The Learned Societies,' coupled with the names of Lord Lister and Professor Michael Foster."

Lord Lister—"Scientific men are not by any means always learned. Their devotion to their special studies often prevents such an occurrence. Nevertheless, I take it that in this toast the Learned Societies are understood to mean the scientific societies, and chiefly those of this metropolis. On this understanding, it seems to me very natural that the person who is asked to respond to this toast should be a representative of the Royal Society, because that Society is the mother of all the scientific societies in London; and while, if I may be allowed to say so, she is herself vigorous and active, she takes a deep maternal interest in the welfare of her offspring. Of her numerous progeny, none, I conceive, discharges her functions more healthily and efficiently than she who is this evening honouring some of her most illustrious and venerable sons. Among these it has been my joy to see my old teacher the venerated and beloved Professor Williamson. The Royal Society, I believe, does good to her daughters, stimulating them to work, and encouraging fruitful intercourse among them: witness, for example, the discovery of argon by the co-operation of Lord Rayleigh and Professor Ramsay. Mr. President, I received from one of your Secretaries an intimation that brevity would be the most valuable quality in any remarks I might make this evening. I gladly act on that suggestion, and will only now tender to you and your Council, on behalf of the representatives of scientific societies, other than the Chemical Society, present here this evening, our warmest thanks for the privilege you have given us of taking part in this memorable celebration. I would also thank Lord Reay for the exceedingly kind terms in which he has proposed the toast, and this illustrious company for the cordial manner in which they have received it."

Professor Michael Foster—"I feel deeply grateful for the very kind words in which Lord Reay has referred to me and my possible future services, in which I trust he may not be disappointed, and for the kind way in which you have received the toast. I perceive the delicate compliment to my physiological acquirements in the inference that, although a President as yet unborn, I can speak. I did not know, in accepting office, that the sweets of office would come thus before their time. I trust that they will be taken off, so to speak, at the other end of the bill. But remembering that all premature utterances, whether vocal or other, are feeble, the more feeble the more premature they are,—and it seems to me that, as President of the British Association, I was conceived the other day,—though I would have wished had not this premature deliverance been coupled with great lateness of the hour, to have turned from an uncertain and dim future to a rich and full past, and to have said something of my experience of these six great men, all of whom I can call my friends, and one of whom—Williamson—taught me not only chemistry but science, I will content myself in saying this, that though I do not know what may be before me as President of the British Association,—do not know what lions, true lions, false lions, there may be in my path,—I

will do my best to make my tenure of office worthy, not only of the Association, but of Science. And may I also give utterance to this wish, in continuance of that international science of which my brother Ostwald spoke, that when the British Association meets at Dover, and the French Association meets at Boulogne, we shall feel that Fashoda is past over, and that we shall not be using the resources of science to make each other as small as we can, but that each will be using the strength of the other to advance the resources of a common knowledge."

"The Guests."

The Treasurer—"I have the honour to propose to you, Fellows of the Chemical Society, that you should drink to the health of your guests. We are favoured here to-night with the presence of a large and distinguished body of gentlemen; how large, and how distinguished, you yourselves may know by a mere glance at the list of their names which is already furnished to you. We are deeply grateful to these gentlemen for the way in which they have responded to the invitation of the Society to be present here to-night to do honour to the gentlemen who are our special guests. Large as the number is, we could well have wished that it was still larger; for our hospitality and our welcome have their physical limits only in the capacity of this room. We could well have wished, for example, that a greater number of our Foreign Fellows were here present. You have heard from the President many messages of congratulation and of good will from certain scientific organisations abroad, and from individual Fellows of our Society. But these messages by no means account for all the kind words, for all the utterances of friendship and felicitation, which have been made in reference to this occasion. I have recently passed through many Continental capitals, and have visited incidentally a number of academic centres, and I have had the pleasure of meeting a considerable proportion of those gentlemen whom we are proud to number amongst our Foreign members. Thus, I have met Franchimont at Leiden, Cleve at Upsala, Waage at Christiania, Pettersson and Arrhenius at Stockholm, Emil Fischer, Landolt, and van't Hoff at Berlin, Liebermann and Witt at Charlottenberg, Ladenburg at Breslau, our active collaborateur Brauner at Prague, our old friend Debus in Cassel, and last, but not least, the *doyen* of the illustrious body, my venerated teacher Bunsen, at Heidelberg. And, gentlemen, I am charged by each and all to convey to you, should I have the opportunity, their heartfelt congratulations on this occasion, and their great regret that circumstances should have prevented them from being here to testify by their presence their appreciation of the great services which these gentlemen whom we especially delight to honour to-night have rendered to Science, and to the Society of which we are so thankful to see them still members. I should like to say an additional word or two about Bunsen. His Excellency has learned to grow old gracefully. He bears the weight of his eighty-eight years admirably. His deafness, it is true, has somewhat increased, and he complained with a touch of pathos which, under the circumstances, has just a suspicion of the element of comedy, that 'he begins to find that his eyesight is not so good as it used to be.' It was for this reason that he asked to be excused from conveying in writing the message which he wished me verbally to transmit to you. I am asked to associate with this toast the name of Mr. Haldane and that of Dr. Böttinger. Mr. Haldane is known to all here for the admirable part he has taken in furthering a cause which many of us have very near at heart—that is, the advancement to its legitimate position of our Metropolitan University. Dr. Böttinger is known to many here as a leading member of a firm whose name is as a household word in the mouths of those who speak of the material and industrial triumphs of our science. Gentlemen, without further word, I give you the health of 'Our Guests,' and I associate with that toast the names of Mr. Haldane, Q.C., M.P., and Dr. Böttinger."

Mr. Haldane—"I confess I feel a little shy in uttering the few sentences which I have to address to you. Previous speakers have come before you with a wealth of distinctions and a profusion of academic tone which it is impossible for me to imitate. Lord Reay, who represents a different branch of the Legislature, has put me to shame by telling me that the House of Lords is 'sound on science.' Well, I am glad to hear it, and I wish I could say as much for the House of Commons. I cannot speak to you as a man of science, nor as a representative of any department of abstract knowledge; I can only speak to you as a humble—that most humble of all functionaries—unofficial member of an Opposition, or what I fear some of you will consider, a battered and shattered fragment of a still more battered and shattered Party. I do not admit, needless to say, the impeachment. I do not regard myself in the least as an atom which has got outside its proper molecule. There is plenty of potential energy in my political combinations. When I was at the University of Göttingen, there was a song we used to sing which ran 'Die Philister sind uns gewogen meist.' Even members of the House of Commons acknowledge the deep debt they are under to-day to science, and perhaps most especially to chemical science. Gentlemen, there was a great victory won the other day in the Soudan. That victory was due to the forethought and skill of a very distinguished soldier; but also to another force. That victory, which pronounced once for all, and finally, the supremacy of mind and trained skill over the most powerful of savage combinations; that victory was won, not merely on the fields before Omdurman, but in the laboratory and the workshop. The smokeless powders, the modern rifling, the bullet of most recent construction, all these are your work. But the obligations which you have rendered us in the past are as nothing to the obligations to which some of us look forward to you in the future. We have spent money lavishly, without a word of complaint from the taxpayer, on the support of the Army and the Navy; but we have not yet spent the money which I believe we ought to spend, and shall be forced to spend, upon the defence of our industries. The country from which Professor Ostwald comes can teach us a lesson. In Germany, where 70 per cent of the upkeep of the universities comes from the Government, they have taught us how to put mind into our work. There are men who would gladly convert the British public to it, but their work is yet to be done. We shall realise these things when the House of Commons will vie with the House of Lords in giving predominance to the great task of diffusing scientific knowledge among our commercial men as among our soldiers. It is with that sentiment in my mind, with that feeling of obligation to these pioneers of the work of the members of this Society, that I gratefully thank you for the toast which has been proposed."

Dr. Böttinger—"Allow me also to thank you most heartily and sincerely for the great honour you have conferred upon your guests by your kind invitation, and by putting them in a position to take part in this beautiful festival on the celebration of six Masters of English Science. Gentlemen, I may also thank you, most especially in my own name, for the great honour you have conferred upon me in mentioning my name specially among the toasts of the evening. I shall not forget this evening; it will always be in my mind a pleasant recollection of what Professor Ostwald said of you. In science we know no bounds and no boundaries internationally, for we are one great common nation. Your esteemed President, Professor Dewar, cordially remarked on the character of the messages you have received this evening from all parts of the scientific world. Allow me to add to these, and assure you that not only from the scientific world, but elsewhere, these feelings are shared with the same heartiness with respect to the great work these gentlemen have done for the development of science and for the benefit of the human race. It is for me a particular pleasure to see by the list of your numerous

members and guests that you also acknowledge that science and industry and technique must go hand in hand; that we who reap the technical part must rely upon the men of science for new ideas and advancement of our work. But I believe and am convinced that the men of science in their connection with us also find new initiative for the furtherance of their ideas; they also find that in connection with the industrial and technical world they see what is further necessary for the development of their work. I am sure that the names of these six illustrious scientific men will be mark-stones in the world for the future, they will be stepping-stones for the new generations. Before I end, allow me to deviate from your English custom, and introduce a custom with us in Germany, a custom which is always followed with great enthusiasm, and to propose now the health of one whom particularly we have to thank for this beautiful evening: it is the health of a man who is a pioneer in science also, and has a great name. I need only remind you of liquefied air. I speak of Professor Dewar, and I ask you to join with me in a hearty three cheers for him. So take your glasses and join with me in our German fashion with Hoch! Hoch! Hoch!

The President—"My Lords and Gentlemen,—I must protest against the intrusion of an additional toast. We have had a most delightful evening; we have achieved our great aim; and I think that the present President is such a nonentity in comparison with the men we are here to honour, that the less said about him the better."

Letters, telegrams, and messages of congratulation were received from the following Foreign Members:—Professor Arrhenius, Stockholm; von Baeyer, Munich; Beilstein, St. Petersburg; Berthelot, Paris; Lecoq de Boisbaudran, Paris; Bunsen, Heidelburg; Cannizzaro, Rome; Cleve, Upsala; Curtius, Bonn; Erlenmeyer, Aschaffenburg; Fischer, Berlin; Fittig, Strassburg; Franchimont, Leiden; Friedel, Paris; Wolcott Gibbs, Cambridge, Massachusetts; Graebe, Geneva; van 't Hoff, Berlin; Körner, Milan; Ladenburg, Breslau; Landolt, Berlin; Liebermann, Berlin; Lieben, Vienna; Markownikoff, Moscow; Mendeleeff, St. Petersburg; Menschutkin, St. Petersburg; Moissan, Paris; Nilson, Stockholm; Pettersson, Stockholm; Rammelsberg, Berlin; Raoult, Grenoble; Remsen, Baltimore; Schlœsing, Paris; Spring, Liège; Thomsen, Copenhagen; Troost, Paris; Waage, Christiania; van der Waals, Amsterdam; Wislicenus, Leipzig; Witt, Charlottenburg, ans from a number of distinguished Fellows and friends of the Society.

A special vote of congratulation was passed by the Russian Chemical Society, and transmitted by Professor Mendeleeff.

"At a meeting of the Russian Chemical Society held this day, it was resolved, that the Society avail itself of the exceptional opportunity of being able to congratulate conjointly Sir Joseph Henry Gilbert, Sir Edward Frankland, Professor Odling, Sir F. A. Abel, Dr. A. W. Williamson, and Dr. J. H. Gladstone, whose distinguished services during half a century stand out as a model for all investigators in Chemical Science, and also express the the wish to see the further results of their labours in the annals of Science for many years to come.

Hon. President, D. Mendeleeff.
Secretary, A. Gorboff.

St. Petersburg, $\frac{20 \text{ May,}}{1 \text{ June,}}$ 1898."

The following telegram was received from the German Chemical Society. "The sister Society sends both Jubilee congratulations and greetings to the Jubilee celebration of the Presidents of the Chemical Society, Gilbert, Frankland, Odling, Abel, Williamson, and Gladstone. The German Chemical Society, C. Liebermann, President."

PHYSICAL SOCIETY.

Ordinary Meeting, December 9th, 1898.

Mr. Shelford Bidwell, F.R.S., President, in the Chair.

Dr. C. Chree read a paper on "*Longitudinal Vibrations in Solid and Hollow Cylinders.*"

The ordinary formula for the frequency of longitudinal vibrations refers to an ideal rod of infinitely small section. This formula constitutes a first approximation, according to which the higher notes are exact harmonics of the fundamental note. Prof. Pochhammer and Lord Rayleigh independently, over twenty years ago, arrived at a corrective term for solid isotropic rods of circular section, according to which the harmonic relation between the notes is no longer exact. During the last twelve years Dr. Chree has devoted several papers to the subject, confirming by independent methods the *results* obtained by Pochhammer and Rayleigh, and arriving at analogous results for other forms of section, and for material symmetrical round an axis but not isotropic. The first part of the present paper develops what appears to be a new method, based on expressions obtained some years ago by the author for the mean values of the strains in an elastic solid of any kind or shape, exposed to any system of forces. Besides confirming his previous results, Dr. Chree obtains new results applicable to material neither isotropic nor symmetrical round the axis of the rod. The second part of the paper treats of a hollow circular rod, or tube, of isotropic material. When the walls of the tube are thin the correction to the ordinary formula is twice as large as for a solid rod of the same diameter. The different methods all point to the conclusion that the ordinary formula supplies a close approximation to the truth only so long as the greatest diameter of the cross section is small compared to the nodal interval in the rod.

A paper on the "*Thermal Properties of Normal Pentane*," by Mr. J. Rose-Innes and Dr. Sydney Young, was then read.

In 1894 the authors investigated the relations between the temperatures, pressures, and volumes of iopentane, through a wide range of volume; the results are published in the *Proc. Phys. Soc.*, xiii., pp. 602-657. It is there shown that if a and b are constants depending on the nature of the substance and on the volume, the relation $p = (bT - a)$, at constant volume, holds good with but small error from the largest volume (4000 c.c. per grm.) to the smallest (1·58 c.c. per grm.). In the neighbourhood of the critical volume (4·266 c.c.), and at large and very small volumes, the observed deviations are well within the limits of experimental error, but at intermediate volumes they are somewhat greater. As they exhibit considerable regularity it is a question whether they could be attributed entirely to errors of experiment. In any case the above relation may be accepted as closely approximate to the truth. The present paper refers to a similar investigation on pure normal pentane obtained by the fractional distillation of the light distillate from American petroleum. The method employed for this separation is fully described in the *Trans. Chem. Soc.* (1897, vol. lxxi., p. 442); the vapour-pressures, specific volumes as liquid and saturated vapour, and critical constants, are given in the same Journal (p. 446). With regard to theoretical deductions from the present results, advantage is taken of the fact that a similar set of experiments had already been carried out with isopentane, which is an isomer of normal pentane. It was hoped that light would be thrown on the question of the influence exerted by difference of chemical structure on the thermal properties of a substance. The conclusion arrived at as most probable is that the coefficients of the second power of the density in the expansion of p must be different for the two substances. The slope of the curve obtained by plotting $(a v^2) - 1$ against $v - \frac{1}{4}$ suggests discontinuity somewhere about vol. 3·4, as with isopentane.

Mr. LEHFELDT asked whether the authors had observed any other singularity or discontinuity at vol. 3·4. He also asked whether the authors were satisfied with ordinary squared-paper in plotting their curves. It ought to be possible to design a machine for doing the work mechanically to 1-50th of a m.m. accuracy.

Mr. APPLEYARD said the fractionating apparatus devised by Dr. Young was a great improvement on older forms; it ensured that there should always be sufficient, and yet not too much, liquid at each valve-trap. He hoped that details of the tube, in the latest form, would be included in the paper. In the separation of such a mixture as chloroform and alcohol, the common method by water-extraction was imperfect; it was not desirable always to convert the mixture wholly into chloroform. Ordinary fractionating tubes yielded an impure distillate in this case. Perhaps the difficulty was inherent for these two liquids. Dr. Young's apparatus would put the question beyond doubt.

Dr. YOUNG, in reply, said that the only objection to curve-tracers was their cost. The curves he had obtained from his experimental results were all isothermals; he did not think isobars would indicate anything such as Mr. Lehfeldt had suggested. With regard to such mixtures as chloroform and alcohol the chances of separation were difficult to predict. A distinction might, however, be drawn between liquids partially miscible and liquids miscible in all proportions. Hexane (b. p. 69° C.) and benzene (b. p. 80° C.), for instance, were both hydrocarbons miscible in all proportions, and it might be thought possible to separate them by a fractionating apparatus; but experiment shows they cannot so be separated. If alcohol and chloroform should turn out to be miscible in all proportions, the probability was that they could not, effectively, be fractionated; if, on the other hand, they prove to behave like partially miscible liquids, the separation by fractionating apparatus such as he had described was rendered possible.

The PRESIDENT proposed votes of thanks to the authors, and the meeting adjourned until January 27th, 1899.

Auriferous Conglomerate of the Transvaal.—G. F. Becker (*Am. Journ. Sci.*).—The auriferous conglomerate of the Witwatersrand gold field constitutes the most important gold deposit ever known. A strip of country a couple of miles in width and about 30 miles in length has yielded since 1887 about 240,000,000 dollars, and only about one-fifteenth of the accessible gold has been extracted. The nature of this wonderful deposit is a subject of manifest interest to geologists and mining engineers, who, however, have arrived at various conclusions. No considerable doubt exists that the conglomerate is a marine littoral deposit, but some observers have held that the gold is detrital, being an original part of the conglomerate; others that it is a chemical precipitate from the ocean in which the pebbly beds were laid down: and still others that the precious metal reached the uplifted but uncemented gravel in solution, so that the ore-bearing strata are allied to ordinary veins. After presenting all the more striking facts which it is necessary to consider in testing the theories propounded to account for the deposition of gold on the Rand, the author rigidly tests each theory by the facts, and reaches the conclusion that the deposition of the gold was in no sense chemical, that there are no valid objections to the theory of marine placer origin, and that no noteworthy features are left unexplained by this theory. The argument is so clear and cogent that the detrital theory of the Transvaal gold may be regarded as firmly established.—*Journal of the American Chemical Society*, vol. xx., No. 9.

NOTICES OF BOOKS.

Technical Mycology: the Utilisation of Micro-organisms in the Arts and Manufactures. By Dr. FRANZ LAFAR. Translated by C. T. C. SALTER. Vol I. "Schizomycetic Fermentation." With 1 Plate and 90 Figures. Pp. 405. London: Charles Griffin and Co. 1898.

THE excellent volume now before us deals entirely with bacteria, both useful and harmful, more especially with regard to fermentation in distilling and brewing, in the preparation of wines and vinegar, in dairy work and farming, &c.

This volume is divided into nine sections and thirty-eight chapters.

In the introduction, the theory of spontaneous generation is discussed, and we find the author seems rather inclined to the opinion that it is simply *unproven*, but not *impossible*.

The earlier chapters deal with the forms of growth, dimensions of bacteria, the structure and constitution of the cell, reproduction, germination, &c. There are three types of germination. In the first type, the spore gradually acquires the normal dimensions and functions of the vegetative form by absorbing liquid from the surrounding medium; it soon divides and reproduces by fission. In the second type, the contents of the spore elaborate into a new rod surrounded by a thin membrane, and eventually bursts the spore capsule at the point of least resistance at the poles; the capsule then shrinks at once to its original size and disappears by dissolving in the surrounding liquid. In the third type, the spore membrane does not burst at the poles, but along a line corresponding with the equator of the spore.

Section II. deals with the general biology and classification of bacteria. The mutual influence of two or more species may be of such a nature that it is impossible for them to live together—the presence of one species retarding the growth of, or even killing, the other. A number of examples of such cases are given throughout the book.

Section III. treats of sterilisation and pure cultures, and Section IV, with chromogenic, photogenic, and thermogenic bacteria. Some bacteria are capable of withstanding prolonged heating without being killed, such as the *Schizomycetes*, which can withstand boiling water for several hours. These, and various other kinds, are dealt with in Section V. The preservation of milk, meat, eggs, vegetables, and fruit is also thoroughly gone into. Lactic fermentation and allied decompositions form the subject-matter of Section VI.

Decompositions and transformations, such as the phenomena of putrefaction, the fermentation of cheese, and the fixation of free nitrogen by bacteria make up Section VIII. The discovery of leguminous nodules was one of very great importance to agriculture. These growths are now being cultivated artificially, and applied direct to the soil as manure.

Section IX., on oxidising fermentations, the iron, sulphur, and nitrifying bacteria, acetic fermentation, and the oxidases, brings the volume to a close

There is a copious table of contents, but we regret to see that there is no alphabetical index.

The preface, written by Dr. Emil Ch. Hansen, bears testimony to the discernment and ability with which the book has been compiled: we are glad to endorse the opinion therein expressed.

The Living Organism: an Introduction to the Problems of Biology. By ALFRED EARL, M.A., late Scholar of Christ Church College, Cambridge; of the Inner Temple, Barrister-at-Law. London: Macmillan and Co., Lim. New York: The Macmillan Company.

THE author, addressing himself to the student of biology, urges the importance of the science and its influence upon

current thought, observing that "inaccurate conclusions and unsound speculation have more serious issues in the case of biology than in any other of the natural sciences," and as security against this, points out the necessity of great care in instruction in the rudiments, and warns the student against taking too much for granted. The character of the work is critical; and the real object, as stated by the author, is to direct attention to the important truth that, "though chemical and physical changes enter largely into the composition of vital activity, there is much in the living organism that is outside the range of these operations."

The subject is treated in a masterly manner, and will repay close perusal by one seriously entering upon scientific investigation in any of its branches, particularly those included under the name of biology.

The matter is not suitable for abstraction, but the concluding sentence is very characteristic of the whole:—"Every branch of research leads sooner or later to the unknowable, and that stage is soon reached in attempting to pursue the mechanical conception of life."

In the present volume, as in a previous work, great pains have been taken to impress the student with the value of thinking for himself.

The subjects are well and clearly arranged, and there is a good index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 11, September 12, 1898.

Crystallisation of the Anhydrous Sulphides of Calcium and Strontium.—M. Mourlot.—Proceeding in the same manner as for the preparation of crystalline barium sulphide, the author has succeeded in obtaining calcium and strontium sulphide, anhydrous and crystalline. A mixture of calcium or strontium sulphate and carbon, or the amorphous sulphide prepared according to Sabatier's method, is submitted to the action of the electric furnace. The crystalline sulphides thus obtained are more stable than the corresponding amorphous sulphides, and less easily attacked by the various reagents. Under the action of carbon at a very high temperature, they are converted into carbides.

A Double Carbide of Iron and Tungsten.—P. Williams.—When a mixture of tungstic acid, iron, and carbon are allowed to react on one another at the temperature of the electric furnace, the mass obtained has a metallic appearance, and is of a complex nature. It consists of carbide of tungsten (WC), probably a carbide (W_2C), and several double compounds of tungsten and iron, one of which the author has isolated and examined. This compound is separated from the whole mass by treating the latter with hot strong hydrochloric acid. The action is rapid at first, but falls off owing to the crystalline residue covering and protecting the bulk of the mass. Frequent grinding is therefore necessary. A crystalline powder is left, formed of two double carbides of iron and tungsten; the simple tungstic carbide and graphite. The double carbide can be separated by means of a magnet, it being highly magnetic. Analysis shows it to have the composition $2Fe_3C.3W_2C$.

Commercial Extraction of Thoria.—G. Wyrouboff and A. Verneuil.—The authors have already announced a very exact method for separating thoria from all the other rare earths which usually accompany it. This method, based on the use of hydrogen peroxide, led to a commercial extraction which is both simple, rapid, and cheap, since it extracts the whole of the thoria in a given mineral in a pure state. This method was applied to several tons of monazite, and gave very satisfactory results. The great advantage of using peroxide of barium is that the precipitated mass contains all the thoria and impurities which do not exceed one-third of its weight.

Constitution of Natural Earthy Substances.—G. André.—Nitrogen in the soil occurs in a soluble form, chiefly as nitrate. This is produced at the expense of so-called organic nitrogen under the influence of the nitric ferment and in presence of a base. Organic nitrogen proceeds from slow vegetable decay or the fixation of free nitrogen by certain micro-organisms. By treating vegetable earth either with alkalis or dilute acids, the nitrogenous matter can be gradually resolved into soluble form, and from the results obtained, Berthelot and André have concluded that the nitrogenous matter of the soil behaves like an amide. The author points out that this nitrogenous matter exists in many different forms, as the result of experiments on four specimens of earth. In order to obtain comparable results, a known weight of each substance is treated similarly, viz.:—(1) Treatment with caustic potash, and subsequent treatment of the insoluble residue with hydrochloric acid; and (2) the inverse process. The results of estimation of the nitrogen are tabulated as percentages of the total amount of nitrogen present in each of the original substances. From these numbers, deductions are drawn as to the ratio in which the different forms of nitrogen occur in the specimens analysed.

No. 12, September 19, 1898.

This issue contains no chemical matter.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xix.-xx., No. 9.

The Solubility in Water of Tricalcic Phosphate and of Apatite.—Jules Joffre.—Already inserted.

New Method of Fractionating the Yttric Earths.—G. Urbain.—Already inserted in full.

Nature of the Didymium which accompanies Yttria from the Monazite Sands. — G. Urbain.— Already inserted in full.

On Neodymium.—O. Boudouard.—Already inserted in full.

Compound obtained with Nitrate of Mercury and Trimethylcarbinol.—G. Denigès.—Already inserted.

Preparation and Etherification of Dissymmetric Dimethylsuccinic Acid. — E.-E. Blaise. — Already inserted.

Action of Aniline and of Phenylcarbamide on the Ketonic Acids of the Series $C_nH_2N—10.O_3$.—T. Klobb.—A long paper, not suitable for abstraction.

Some Interesting Experiments on the Synthesis of Estragol and the Allylic Essences.—Ch. Moureu.—The author, with M. Tardy, heated over a water-bath iodide of allyl and anisol in the presence of powdered zinc. A violent reaction took place, and vapours of iodine were given off, and iodide of methyl, anisol, phenol, and a mixture of various other compounds passed over on distillation after treatment with dilute soda and being fractionally distilled. Between 200° and 210°, a liquid body is collected still containing traces of iodine, of which the elementary composition is sensibly different to that of estragol. The author then had recourse to the method of Friedel and Crafts, based on the curious properties of chloride of aluminium; and by the help of that method he obtained a small portion of a liquid having decidedly the smell of estragol, but the quantity was too small for further isolation.

Thermochemistry. Quinoleic Bases and Hydrides: Salts.—Marcel Delèpine.—Quinoleic bases are generally prepared by the action of a primary aromatic amine on an aldehyd, an acetone, or a substance susceptible of giving rise to one of these functions. Hydrogen is not given off; it either acts on the quinoleic base, forming a hydride, or on the aldehydic or acetonic body, or on an oxidising auxiliary used in the reaction. The author has studied this reaction from the thermochemical point of view, using quinolein, quinaldine, and their tetrahydrides. He has also studied the basicity of these compounds with regard to hydrochloric acid, and has obtained five compounds.

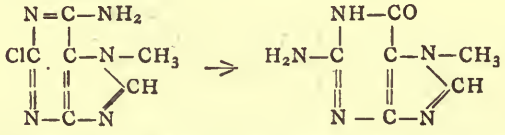
The Sugar in Orange-peel.—J. Flatau and H. Labbé. —Already inserted.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xxxi., March 28, 1898.

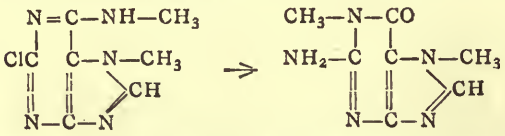
On Racemy.—A. Ladenburg.—The author has given the name of partial racemy to the following phenomenon. Salts which form certain acids enclosing an asymmetric carbon with active base, give by decomposition an inactive acid at certain temperatures and an active acid at other temperatures.

The Racemisation of Acid Malate of Ammonium. —J. H. van't Hoff and H. M. Dawton.—Pasteur showed that when solutions of acid malate of ammonium are left alone at about 70° they deposit, first, crystals of active malate, and the mother-liquor then contains a hydrated racemic salt. Below 70° only racemic salts are obtained. The authors have determined the exact conditions of temperature, &c., under which this transformation takes place.

Molecular Transformation in the Group of Purines. —E. Fischer.—The author shows that warm dilute alkalies transform methyl-γ-amino-6-chloro-2-purine into methyl-γ-guanine—



This reaction can be explained by an internal molecular transformation, but the author prefers to admit a momentary rupture of the nucleus. To prove this hypothesis he has effected the same transformation with methyl-γ-methylamine-6-chloro-2 purine and obtained the corresponing dimethylguanine—



These reactions are easily done by heating the chlorinised derivative to 100° for two hours with a large excess of water and a small quantity of soda.

A Synthesis of Diphenylhydantoïn.—W. Hentschel. —Phenylhydantoïn was prepared by saturating a benzoic solution of phenylglycocol with $COCl_2$; this gives rise to a corresponding chlorocarbonate—

$$C_6H_5-NH-CH_2-CO_2H_5+COCl_3 = \\ = C_6H_5-N\begin{matrix}COCl\\ CH_2CO_2C_2H_5\end{matrix} + HCl.$$

Aniline reacts on this body when warm, giving—

$$C_6H_5.N\begin{matrix}CO.NH.C_6H_5\\ CH_2CO_2C_2H_5\end{matrix}$$

Repeated crystallisations transform this product into diphenylhydantoïn—

$$C_6H_5.N\begin{matrix}CO.NH.C_6H_5\\ CH_2CO_2C_2H_5\end{matrix} = \\ = C_6H_5N\begin{matrix}-CO-\\ CH_2-CO\end{matrix}N.C_6H_5+C_2H_5OH.$$

Preparation of the Acetals of the Ortho-substituted Aromatic Aldehyds.—E. Fischer and G. Giebe.— In applying their process for the preparation of acetals to the *o*-substituted aromatic aldehyds, the authors have studied the influence of neighbouring groups on the speed of the reaction; the electro-negative radicals (Cl, NO_2, &c.) accelerate it slightly, and the electro-negative radicals (CH_3, &c.) retard it. They have prepared a number of acetals by leaving the aldehyd in contact with an excess of alcohol containing 1 per cent of hydrochloric gas for twenty-four hours; these acetals are all described and their formulæ given.

MISCELLANEOUS.

Coating Iron and other Metals with Lead.—E. v. Münstermann.—The object is first cleaned with a brush soaked in petroleum, then dried, and placed in a lead-lined bath containing dilute nitric acid. After drying, it is plunged into a mixture of sulphuric acid, urine, and water, and left until all trace of rust has disappeared. After this, the object is immersed in a mixture of hydrochloric acid, water, and double iodide of mercury and potassium, to facilitate the adherence of the lead. It is finally dipped in melted lead. For forged objects, the temperature of the lead bath should be at least 470° C.; but for castings it should be much higher.—*Ackermann's Gew. Zeit.*, xxiv., [3], p. 21.

Royal Institution.—The following are the lecture arrangements at the Royal Institution before Easter:—Sir Robert Ball, six lectures (adapted to young people) on "Astronomy"; Professor E. Ray Lankester, ten lectures on "The Morphology of the Mollusca"; Mr. A. Henry Savage Landor, three lectures on "Tibet and the Tibetans"; Dr. Allan Macfadyen, four lectures on "Toxins and Antitoxins"; Mr. William Poel, three lectures on "English Playhouses in the 15th, 16th, and 17th Centuries"; Sir Alexander Mackenzie, three lectures on Liszt, Tschaikowsky, Brahms" (with musical illustrations); The Rt. Hon. Lord Rayleigh, seven lectures on "The Mechanical Properties of Bodies." The Friday Evening Meetings will begin on January 20th, when a Discourse will be delivered by Professor Dewar on "Liquid Hydrogen"; succeeding Discourses will probably be given by the Right Hon. Sir Mountstuart E. Grant Duff, Mr. Victor Horsley, Professor H. S. Hele-Shaw, Mr. Richard R. Holmes, Sir Frederick Pollock, Bart., Professor H. L. Callendar, The Right Hon. Lord Rayleigh, and other gentlemen. The year 1899 is the Centenary Year of the Royal Institution, and arrangements are being made with a view to its celebration in a fitting manner. Details will be announced at a later period.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Microscopical, 7.30.—Exhibition of Binocular Microscopes.

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THE CHEMICAL NEWS.

VOL. LXXVIII., No. 2039.

THE ORIGIN OF THE GASES EVOLVED ON HEATING MINERAL SUBSTANCES, METEORITES, &c.*

By MORRIS W. TRAVERS, D.Sc.

THE study of the gases evolved on heating mineral substances has been made the subject of a number of investigations, and the results have formed a basis for speculations as to the origin and history of these substances.

In a paper entitled "The Gases enclosed in Crystalline Rocks and Minerals,"† Professor Tilden has suggested a theory to account for the evolution of gases by mineral substances under the influence of heat. He considers that the gases, which are given off on heating certain rocks and minerals, are actually present in those substances in the gaseous state, enclosed in small cavities under high pressure. To account for their presence in these cavities he makes the suggestion, "that the rock crystallised in an atmosphere rich in carbon dioxide and steam, which had been, or were at the time, in contact with some easily oxidisable substance, at a moderately high temperature. Of the substances capable of so acting, carbon, a metal, or the protoxide of a metal, present themselves as most probable."

Beyond the fact that minerals give off gases when heated, there is, except in the case of carbon dioxide, no direct experimental evidence to show that these substances really contain the gases in the free state. In many cases no cavities can be seen in thin sections of the mineral, and as a mineral yields about the same quantity of gas when ground to a fine powder as when it is only broken into small pieces, the cavities must be assumed to be very minute if they exist at all. I do not contend that it is impossible for a rock to contain considerable quantities of gases enclosed in cavities, but I propose to prove experimentally that—at least in some cases where a mineral or rock yields gases other than carbon dioxide on heating—those gases are produced during ignition, by the interaction of its non-gaseous constituents. I shall first consider the formation of carbon monoxide and hydrogen from minerals and rocks which contain as active constituents only water, carbon dioxide, and ferrous oxide.

A glance through the results of the analyses of some such substances, and of the gases evolved by heating them, will show that the quantity of hydrogen and carbon monoxide produced bears a certain relation to the quantity of ferrous oxide and to the quantity of water given off on heating the substance. In the following table the quantities of ferrous oxide and water are expressed in terms of weight *per cent.*; the gases in cubic centimetres per grm. of mineral.

Mineral.	Locality.	FeO.	H_2O	H_2.	CO.	CO_2.
Chlorite ..	Zoptan, Moravia	10·6	4·6	2·180	0·494	0·123
Serpentine‡	Zermatt	2·7	9·5	0·800	none	none
Gabbro ..	Isle of Skye ..	6·1	1·5	0·490	none	none
Mica	Westchester, Pennsylvania	1·4	0·13	0·08		0·150
Foliated talc§	Greiner, Tyrol	0·4	4·5	0·04		0·070
Felspar‖ ..	Peterhead ..	2·1	1·00	0·214		1·201

* A Paper read before the Royal Society, November 24, 1898.

† *Roy. Soc. Proc.*, vol. lx , p. 453.

‡ Analysis by Miss E. Aston, *Quart. Journ. Geol. Soc.*, 1896, lii., p. 456.

§ The talc lost only 0·06 per cent of water when heated in the hard glass tube; remainder came off at a very bright red heat.

‖ The felspar contained free iron.

The estimation of the ferrous iron was conducted in the following manner:—The sulphuric acid (30 per cent), previously boiled and cooled in a corked flask, was poured into the bottom of a thick-walled glass tube. The mineral was weighed out into a small test-tube with a glass rod sealed to the bottom of it to support it above the sulphuric acid in the large tube during exhaustion. The tube was drawn out at the end as in fig. 1, attached to a

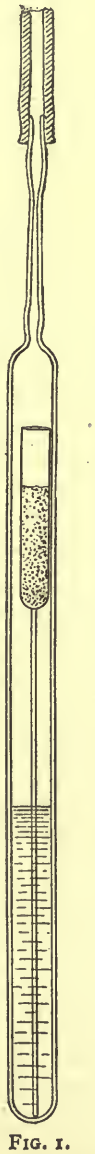

FIG. 1.

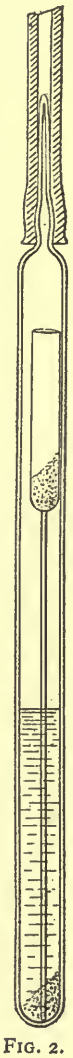

FIG. 2.

Töpler pump by a rubber tube, exhausted, and sealed at the capillary. After heating to 170°—till the mineral was entirely decomposed—the tube was again attached to the pump as in fig. 2, the point of the capillary was broken inside the rubber tube, and the gas contained in it was pumped out and analysed. The tube was afterwards cut open, and the ferrous sulphate was estimated by titration with a solution of potassium permanganate. In the case of the mica it was necessary to use strong sulphuric acid to decompose the mineral.

In general, the gas contained in the sealed tube con-

sisted only of carbon dioxide. In the case of the felspar from Peterhead granite, and of certain helium-yielding minerals, the gas also contained hydrogen. I shall deal with these minerals separately.

That the minerals, which on heating give hydrogen and carbon monoxide, give neither of these gases when decomposed by means of dilute sulphuric acid, is almost sufficient evidence to show that the gases are not present in the minerals in a free state, *either occluded* or enclosed in cavities. That the amount of hydrogen and carbon monoxide produced by heating a mineral is, as I have shown, proportional to the amount of ferrous oxide, water, and carbon dioxide present in it, may be taken as evidence that the gases are produced by the interaction of these substances when the mineral is heated, according to the equations—

$$2FeO + H_2O = Fe_2O_3 + H_2$$
$$2FeO + CO_2 = Fe_2O_3 + CO.$$

If this is the case, the mineral, after ignition *in vacuo*, should contain less ferrous oxide than it did originally; the difference between the quantities of ferrous oxide before and after heating should be equivalent to the hydrogen and carbon monoxide evolved; and these may be calculated from the equations written above.

One c.c. of hydrogen or carbon monoxide is equivalent to 0·006428 grm. of ferrous oxide.

In order to prove this experimentally, I selected a chlorite from Zoptan in Moravia. This mineral contained 10·60 per cent of ferrous oxide, 4·79 per cent of water, and consequently gave a considerable quantity of hydrogen on heating. It was also quite free from sulphides, which seriously interfere with the accurate estimation of ferrous oxide.

A weighed quantity, about 10 grms., of the chlorite was heated in a hard glass tube till it ceased to give any gas. The gas was collected and analysed, and the loss of weight of the mineral was determined by weighing the hard glass tube before and after heating.

Analysis of gas expressed in cubic centimetres per gramme:—

CO_2	0·123
CO	0·094
H_2	2·180

Loss of weight on heating, 4·79 per cent.

The mineral was allowed to cool *in vacuo* to prevent the oxidation of the ferrous oxide. The ferrous oxide was estimated in a sample of the mineral before and after heating.

Ferrous oxide in mineral before heating:—

(*a*) 10·62 per cent; (*b*) 10.60 per cent; mean, 10·61 per cent.

Ferrous oxide in mineral after heating:—

(*a*) 9·70 per cent; (*b*) 9·61 per cent; mean, 9·65 per cent.

But since the mineral lost weight to the extent of 4·79 per cent on heating, a correction must be applied.

Ferrous oxide in mineral after heating corrected for loss of weight of mineral ..	9·18 per cent
Difference in amount of ferrous oxide present in mineral before and after heating ..	1·43 „

The amount of ferrous oxide oxidised to ferric oxide can also be calculated from the quantities of hydrogen and carbon monoxide collected.

2·180 c.c. per grm. of hydrogen is equivalent to	1·401 per cent of FeO
0·094 c.c. per grm. of carbon monoxide is equivalent to	0·057 „ „
Total..	1·458 „ „

This number agrees very closely with that already obtained.

The application of this method of investigation is very limited, as it is difficult to obtain minerals which are quite free from sulphides and carbonaceous matter, and which at the same time give on heating a sufficient quantity of carbon monoxide and hydrogen. Other specimens of chlorite gave large quantities of hydrogen on heating, but they were found to contain sulphides.

The minerals and rocks which had been investigated up to this point, had all been of igneous origin. At Professor Bonney's suggestion, I next proceeded to determine whether minerals of aqueous origin, containing ferrous oxide, water, and carbonates, would give hydrogen and carbon monoxide on heating. Professor Bonney kindly obtained for me a specimen of chalk marl, rich in glauconite, from the Cambridge beds.

The glauconite was freed from chalk as far as possible by washing with dilute hydrochloric acid. The residue, seen under the microscope, appeared to consist of foraminiferous casts, with adhering grains of glauconite. The sample taken for the experiment contained 1·33 per cent of ferrous oxide, 15 per cent of water, and 13·7 per cent of calcium phosphate.

Heated in a hard glass tube to a dull red heat for some time, only 5·7 per cent of the water was given off with a considerable quantity of gas, which was found on analysis to have the following composition:—

CO_2	4·518 c.c. per grm.
H_2	3·128 „
CO	0·083 „
CH_4, &c.	0·204 „

On heating to a bright red heat in the flame of a Bunsen burner, the remaining water and more gas was given off:—

CO_2	13·38 c.c. per grm.
H_2, &c.	0·25 „

The greater part of the hydrogen and hydrocarbons is probably produced by the breaking down of organic matter in the mineral. This organic matter may be due to infiltration from the surface, but, considering the treatment the mineral had received, it is more probably contained in the formaniniferous casts, the decomposition products of their original occupants.

The presence of manganous oxide in minerals appears also to favour the production of hydrogen and carbon dioxide; indeed, it has long been known, that when moist manganous carbonate is heated, these gases are always produced along with carbon dioxide.

The first reactions which take place when the mineral is heated, may be expressed by the equations:—

$$MnO + H_2O = MnO_2 + H_2.$$
$$MnO + CO_2 = MnO_2 + CO.$$

But it was found that when cerite, a mineral which contains a considerable quantity of manganous carbonate, was heated, the gas contained not only hydrogen, but oxygen, the product of a reaction taking place at a somewhat higher temperature:—

$$3MnO_2 = Mn_3O_4 + O_2.$$

Analysis of the gas obtained by heating finely-powdered cerite gave the following results:—

CO_2	15·0 (about) c.c. per grm.
CO	1·554 „
H_2	3·905 „
O_2	0·406 „

A cobalt ore containing only the higher oxides of manganese gave about 10 c.c. of oxygen per grm. of minerals (*Roy. Soc. Proc.*, lx., p. 444).

Yttrotantalite, samarskite, &c., containing lower oxides of uranium, also give small quantities of hydrogen when heated. The hydrogen may be produced according to the equation—

$$3UO_2 + 2H_2O = U_3O_8 + 2H_2.$$

The quantity of hydrogen is not, however, very large.

Minerals containing sulphides usually give a mixture of hydrogen, sulphuretted hydrogen, and sulphur vapour when heated. The quantity of gas is often very large, but the reaction is too complicated for direct investigation. It is probable that the sulphides react with water, forming sulphuretted hydrogen, which at the temperature of the reaction is decomposed into sulphur and hydrogen.

It is known that certain crystalline minerals contain liquid hydrocarbons enclosed in cavities. It is also possible that the methane, and other hydrocarbons sometimes present in the gases obtained by heating mineral substances, may be produced by the destructive distillation of bituminous matter infiltrated into it, or from vegetable matter, particularly if the specimen has been long exposed on the surface.

Nitrogen I have only rarely obtained by heating minerals. Malacone (*Roy. Soc. Proc.*, 1897, vol. lx., p. 444) yields it in larger quantity, compared with the total quantity of gas evolved, than any other mineral which I have examined, but even in that particular case only a very small quantity of the gas is obtained. It is possible that a finely powdered mineral may on standing condense air on its surface. Dr. G. McGowan tells me that when a sample of china clay was heated in a current of hydrogen a small quantity of ammonia was given off. Certain bituminous shales, in which the organic matter is certainly of animal origin, are known to contain large quantities of ammonium salts; the gases evolved under the influence of heat would certainly contain nitrogen. Nitrogen and its oxides might also be the product of the interaction at a high temperature of nitrates infiltrated into the rock and silica. That Davy obtained nitrogen from quartz is highly improbable. It is more likely that the gas was introduced accidentally in the course of the experiment.

I stated earlier in this paper that the felspar from Peterhead granite exhibited certain peculiarities, and that I should describe it separately. The granite consisted of very large crystals of quartz and felspar, with a comparatively small quantity of mica of a dark colour. On heating, a mixture of carbon dioxide, carbon monoxide, and hydrogen was driven off.

In order to ascertain whether these gases were derived from each of the minerals, or whether any particular one gave more gas on heating than the others, I crushed a large quantity of the granite in an iron mortar and picked out the constituents, separating them from one another as far as possible. The mica was easily obtained quite pure, but the quartz and felspar could not, without very great trouble, be separated from one another; in fact, the felspar always contained a considerable quantity of the latter mineral.

By heating weighed quantities of the component minerals to red heat in hard glass tubes, and collecting and analysing the gases, the following results were obtained. The results are expressed in cubic centimetres of gas per grm. of mineral:—

	Quartz.	Mica.	Felspar.
Carbon dioxide	0·225	none	0·172
Carbon monoxide .. }	0·074	none	0·059
Hydrogen .. .. .. }		0·164	0·218

These results show that the mica and felspar are responsible for nearly the whole of the hydrogen, while the greater part of the carbon dioxide is derived from the quartz. The carbon dioxide is probably present in cavities in the quartz, but if the hydrogen were also present in cavities, one would expect that it would be also obtained in greatest quantity from the quartz, the only mineral of the three which has no cleavage; one would not certainly expect to obtain it from the mica.

As the felspar gave off gas in the cold when treated with dilute sulphuric acid, a weighed quantity of the mineral was placed in a thick-walled tube, with a second tube containing 50 per cent sulphuric acid. The tube was drawn to a point, exhausted, and sealed in the manner already described. After heating for twenty-four hours to 170° the gas was pumped out and analysed, and the ferrous sulphate in the solution was determined.

The following results were obtained from two samples of felspar from different parts of the same block of granite. The quantities of gas are expressed in cubic centimetres per grm.:—

	(*a*)	(*b*)
Ferrous oxide in solution	4·02 p.c.	2·05 p.c.
Hydrogen with trace of hydrocarbon	3·50 ,,	1·99 ,,
Carbon dioxide	0·20 ,,	0·90 ,,

From these results I was led to suppose that the felspar contained both free iron and ferrous oxide, since, if we calculate the amount of iron which would be equivalent to the hydrogen evolved, we find that expressed in terms of ferrous oxide:—

3·50 c.c. of hydrogen per grm. = 2·25 per cent of ferrous oxide.

1·99 c.c. of hydrogen per grm. = 1·23 per cent of ferrous oxide.

Quantities which are considerably less than the quantity of ferrous oxide found by titration. On the other hand, it is possible that some of the hydrogen is taken up by the ferric compounds present, lessening the yield of hydrogen, and increasing the quantity of ferrous sulphate in the solution.

There is, unfortunately, no accurate method of estimating the free iron in minerals. The copper method apparently fails in the presence of hydrated ferric oxide, on account of the secondary reactions which take place between that compound and copper sulphate, and subsequently between the ferric sulphate and precipitated copper.

In order to prove that a considerable amount of free iron was present in the felspar, two weighed quantities of felspar from the same sample were heated with 50 per cent sulphuric acid and 96 per cent acid respectively. The gases were subsequently pumped out of the tubes and analysed, and the ferrous sulphate was estimated in the liquid.

The following results were obtained:—

(*a*) With strong sulphuric acid, carbon dioxide and sulphur dioxide .. 1·26 c.c. per grm.
Hydrogen and trace of hydrocarbons .. .. 0·49 ,,
Total .. .. .. 1·75 ,,
Ferrous oxide .. .. 2·07 per cent.

(*b*) With 50 per cent sulphuric acid, carbon dioxide .. .. 0·23 ,,
Hydrogen and trace of hydrocarbons .. .. 1·64 ,,
Total .. .. .. 1·87 ,,
Ferrous oxide .. .. 2·26 per cent.

These figures indicate that the sulphur dioxide and hydrogen produced by the action of the strong acid is just equivalent to the hydrogen produced by the dilute acid, indicating that the felspar contains metallic iron, which is probably the source of the whole of the hydrogen evolved when the mineral is treated with acid. The hydrogen and carbon monoxide given off on heating the felspar are produced by the action of water and carbon dioxide on ferrous oxide and metallic iron present in the mineral.

Both the gas obtained by heating the felspar and gases obtained from the sealed tube experiments contained traces of hydrocarbon. This may be accounted for on the assumption that the free iron in the felspar contains a small quantity of carbide.

(To be continued).

NOTES UPON THE SYNTHESIS OF ETHYL ALCOHOL.

By FRANK WOOD.

ACCORDING to the text-books, with their proverbial self-assurance, it is quite an easy matter to synthesise ethyl alcohol. We are told that all that is necessary is to convert acetylene (made by sparking across two carbon points in an atmosphere of hydrogen) into ethylene by means of nascent hydrogen, or by passing a mixture of acetylene and hydrogen through a red-hot tube; the ethylene so produced is then passed into hot concentrated sulphuric acid, and the ethyl sulphuric acid thus formed on distillation with water yields ethyl alcohol.

I have performed the following experiments in order to synthesise alcohol; assuming, however, that acetylene can be obtained synthetically by the electrical sparking process, I made my acetylene by other methods.

1. Acetylene, generated from calcium carbide by the action of water, was then mixed with hydrogen in a large tube filled with $CaCl_2$, and the mixed gases were then passed through 18 inches of red-hot combustion tubing containing layers of red-hot woolly asbestos; the effluent gases were received in pure sulphuric acid in potash bulbs, in one case cold and in another heated to 170° C.; in both instances the acid became very dark brown, but neither of the acids, after large dilution with water and distillation, yielded even a trace of ethyl alcohol. The asbestos after the experiment was found to contain a considerable quantity of brownish-black carbonaceous dust, showing that the acetylene and hydrogen had reacted somewhat as follows:—

$$C_2H_2 + H_2 = C_2 + 2H_2.$$

As I was not seeking to prepare carbon or hydrogen, this could scarcely be considered a satisfactory result.

2. Calcium carbide and zinc dust were intimately mixed and put into a suitable generator, dilute sulphuric acid was gradually allowed to enter automatically, and the gases evolved were dried and passed through strong H_2SO_4 heated to 170° C. As in the previous case, the acid became a very dark brown colour, and on dilution and distillation gave no trace of alcohol; it yielded instead rather a fragrant odour of cedar-wood oil, which, however, was not the object of my quest.

3. Text-books strongly recommend copper acetylide, so I next tried to produce ethyl alcohol by its use. This substance in the wet state was ground up to a paste with zinc dust, and the gases evolved by the addition of dilute sulphuric acid were dried and passed through a red-hot tube into pure H_2SO_4 at 160 to 170° C. The usual results—that is, the enormous production of black carbonaceous substance and a dirty brown non-ethylated sulphuric acid—were obtained.

4. Relying upon the concise dogmatism of the text-books which state that copper acetylide and zinc dust, when treated with ammonia, give ethylene, I tried an experiment on similar lines to the foregoing, only with the use of ammonia instead of dilute H_2SO_4, and with the abolition of the red-hot tube. In the cold the ammonia produced a considerable supply of gas, which I fear could only be acetylene, as under the same conditions zinc dust gave no evolution of hydrogen. Of course this result was also negative as far as the production of alcohol was concerned, so—whether I used a high or a low temperature, or acetylene with or without nascent hydrogen—no alcohol was obtained in any case.

I have consulted Beilstein, the *Berichte*, the *Journal of the Chemical Society*, and a number of chemical journals and text-books, but so far have not been able to meet with an article by the original person whose statements have since inspired a whole succession of text-book writers; possibly some of your readers may be able to throw some light upon a subject which to me appears inscrutable.

ON A

GENERAL METHOD FOR THE PREPARATION OF MIXED CARBONIC ETHERS OF THE FATTY AND AROMATIC SERIES.

By P. CAZENEUVE and A. MOREL.

BY causing chlorocarbonate of ethyl to react on the sodic or potassic phenols, Fatianow (*Jahresb.*, 1864, p. 477), Richter (*Journ. f. Prakt. Chem.*, Series 2, xxvii., pp. 503 and 511), and Bender (*Deutsch. Chem. Gesellsch.*, 1880, p. 696), obtained mixed carbonic ethers of ethyl and various phenols. We have succeeded in preparing these mixed carbonates in a different and more practical manner, *by heating neutral phenolic carbonates in the presence of certain organic bases, in different alcohols.* Carbonate of phenyl in particular—

$$CO{<}^{OC_6H_5}_{OC_6H_5},$$

heated with urea in various homologous alcohols of the fatty series, gives mixed carbonates of phenyl and these different alcohols. We have thus been able to obtain good returns of the mixed phenylic carbonic ethers; of methylic, ethylic, propylic, secondary propylic, isobutylic, and isoamylic alcohols, and even the carbonate of phenyl-allyl.

With the exception of phenyl ethyl, these ethers were hitherto unknown. Some of these ethers were obtained in a very pure state, and gave good results on analysis. Some others, in proportion as they rise in the series of alcohols, are more difficult to purify, on account of the formation of allophanates and urethanes; which pass over even when distilled *in vacuo*.

Other bases act in the same manner as urea, without giving rise to these inconvenient impurities. In this way aniline, sulphanilate of soda, dimethylaniline, pyridine, quinolein, and dimethyl piperazine when heated with carbonate of phenyl to boiling-point for several hours in the presence of a large excess of ethylic alcohol, give carbonate of ethyl and phenyl.

Turning to the other carbonates of phenol, carbonates of gaïacol, thymol, cresol, &c., with various alcohols, we obtain the corresponding mixed carbonates.

The intervention of bases is necessary. The phenolic carbonates heated alone in the alcohols remain unchanged. Carbonate of phenyl, heated to boiling-point for several days in alcohol at 93°, gives, however, a little mixed carbonate; but the reaction is very slow. The bases stimulate the reaction, and even cause it in the cases of the numerous phenolic carbonates with which we have experimented. Without doubt the action of the bases is to form alcoholates which cause the double decomposition according to the following equation:—

$$CO{<}^{OC_6H_5}_{OC_6H_5} + \underbrace{C_2H_5OH,C_5H_5N}_{\text{Alcoholate of pyridine.}} =$$

$$= CO{<}^{OC_2H_5}_{OC_6H_5} + \underbrace{C_6H_5OH,C_5H_5N}_{\text{Phenate of pyridine.}}$$

The affinity of the base for phenol hastens the decomposition.

Further, the acid-alcohol character of the carbonic acid is not strange to this formation of mixed carbonate; the decomposition takes place preferably on the acid group of the carbonic acid. The alcohol group of the carbonic acid, etherified by phenol, is, according to the regular rule, less saponifiable and much more stable.

As a further proof of the mechanism we have applied to explain the formation of these mixed carbonic ethers, we would draw attention to the very characteristic action of the soda-alcoholates.

The reaction takes place rapidly, and in most cases in

the cold. By adding 1 molecule of ethylate of sodium dissolved in an excess of absolute alcohol, to 1 molecule of carbonate of phenyl dissolved in a mixture of alcohol and ether, we obtain 60 per cent of the mixed carbonate. Care must be taken to moderate the reaction by cooling, otherwise a double carbonate of ethyl will be produced. The reaction takes place according to the following general equation:—

$$CO\begin{matrix}OC_6H_5\\OC_6H_5\end{matrix} + C_2H_5,ONa = CO\begin{matrix}OC_2H_5\\OC_6H_5\end{matrix} + C_6H_5ONa.$$

It is necessary only to arrange the conditions of the reaction for each particular case.

Numerous mixed carbonic ethers from different phenols and alcohols have been thus prepared, and will be shortly described. Sometimes, however, we get a double alcoholic carbonate.

To sum up, this general method is the easiest and most profitable for preparing the mixed carbonic ethers of the fatty and the aromatic series, and consists of making the sodic or potassic alcohol derivatives react on the carbonates of the phenols, or, what is better in certain cases, using alcoholic solutions of organic bases.—*Journ. de Pharm. et de Chim.*, Series 6, vol. ix., No. 2.

THE ESTIMATION OF PERCHLORATE IN CHILI SALTPETRE.

By O. FOERSTER.

THE usual methods for the estimation of the chlorates and perchlorates in saltpetre—methods based on reduction by calcination for two hours at a dull red heat—do not give very exact results. The cause of error rests principally in the volatility of the alkaline chlorides, and partly in the loss of chlorine by the decomposition of these latter. It may also be due to the insufficient reduction of the oxygenated compounds of chlorine. Further, melted saltpetre has an inconvenient tendency to creep over the edge of the crucible, which will occasion losses. To guard against this loss it is necessary to use very large crucibles, and it is not easy to heat them in a uniform manner,

The following process, which is very simple and allows of the rapid and complete reduction of the chlorates and perchlorates, is free from all the objections just mentioned:—10 grms. of the saltpetre to be analysed are mixed with 10 grms. of anhydrous carbonate of soda free from chlorine, and the mixture heated over a strong flame in a covered platinum crucible, or in a large porcelain crucible, until it becomes liquid and no longer gives off gas bubbles; this will not take more than ten minutes. The melted mass does not adhere strongly to the sides, and after cooling is completely dissolved in excess of nitric acid. In the solution thus obtained the total chlorine is estimated in the usual manner. This method leaves nothing to be desired in the way of exactitude.

In a mixture of 10 grms. of nitrate of soda free from chlorine and 10 grms. of anhydrous perchlorate of potash, treated as described above, the following results were found on titrating with sulphocyanide of potassium, by Volhardt's method:—

I. 0·49990 $KClO_4$ = 99·88 per cent of the quantity used.
II. 0·50004 ,, = 100·01 ,, ,,
III. 0·49921 ,, = 99·84 ,, ,,

The following experiment shows that there is no loss of chlorine caused by the decomposition of chlorides and chlorates; in a mixture of 10 grms. of $NaNO_3$ and—

0·1012 grm. NaCl (= 0·06132 grm. of Cl),
0·1012 grm. $KClO_3$ (= 0·02927 grm. of Cl),
0·1006 grm. $KClO_4$ (= 0·02574 grm. of Cl),

the mixture therefore contained a total of 0·11633 grm. of chlorine, and 0·11627 grm. Cl was found,—that is to say, 99·95 per cent of the quantity used.—*Chemiker Zeitung*, 1898, p. 357.

THE SOLUTION OF SOLIDS AND LIQUIDS IN GASES.

By P. VILLARD.

(Concluded from p. 298).

V. *Critical Phenomena.*

IF chloride of ethyl, for example, is put in the presence of compressed formene, we notice that at 200 atmospheres and 17° the surface of the liquid loses its distinctness and becomes transformed into a zone of transition several millimetres thick. On agitation the two fluids form a homogeneous mixture. This phenomenon is in every way similar to that observed when we heat a liquid in a closed vessel up to its critical temperature. We have to deal with a true critical point, as already noticed by M. Cailletet in the case of liquid carbonic acid and air.

The pressure at which the surface disappears varies with the temperature. We can thus observe the phenomenon in two ways: 1st, by raising the temperature and keeping the pressure constant; 2nd, by increasing the pressure while maintaining a constant temperature. For any given gas and liquid there will thus be an infinity of critical points, each corresponding to a definite temperature and pressure.

The explanation of these phenomena is very simple; the solubility of the liquid in the gas increases when the temperature or the pressure is raised. At any given temperature, if the pressure is sufficiently great, formene saturated with chloride of ethyl, for example, will have the same composition as chloride of ethyl saturated with formene, and the two fluids will mix: this is what takes place at 17° under a pressure of 200 atmospheres; with sulphide of carbon and formene, at the same temperature, it is necessary to have a pressure of 550 atmospheres.

The phenomena observed in the neighbourhood of this critical point are exactly similar to those observed in ordinary Natterer tubes; the cause is, however, different, and does not consist, as in these latter, in a want of thermic equilibrium; the results are, in fact, the same when the pressure only is varied.

The formation at the critical point of a zone of transition arises from the fact that the reciprocal saturation of the two fluids can only take place at their surface of separation, unless the diffusion is aided by agitation. It is thus only in the immediate neighbourhood of the surface that the liquid and the gas can become of the same density; it is no longer so at a little distance away: this causes a continuous variation of the density, and of the index of refraction along the whole length of the tube. The analogy with liquefied gases is again met with in the appearance caused by condensation. If, for example, the pressure is lowered in a tube containing two fluids previously brought to the critical pressure, a simultaneous boiling and rain takes place; the resemblance with what takes place near the critical temperature in a Natterer tube which is cooled is complete. This phenomenon is easily explained; by releasing the pressure the liquid gives up a part of the dissolved gas, and *vice versâ*.

VI. *Applications.*

The use of gaseous solvents furnishes a new solution of the problem of the distillation of bodies decomposed by heat. As a rule we have recourse to a vacuum when dealing with bodies of this nature; their boiling-point can then be sufficiently reduced that, as a rule, decomposition need not be feared; but this process cannot evidently be applied to bodies so little volatile as stearic acid for in-

stance. Another inconvenience of this method is, that at a low temperature the vapour tension is often very much reduced. The vaporisation, it is true, is very active, but each litre of vapour represents only an insignificant quantity of material.

There would be a very great advantage in substituting for distillation, solution in a suitable gaseous medium. This is equivalent to considerably augmenting the volatility of the substance in question. By reducing the pressure of the atmosphere the whole of the substance dissolved would be deposited, the dissolving power of the gas becoming practically *nil*. This is a very great advantage over liquid solvents. The most volatile bodies being at the same time the most soluble, an operation of this character would give results analogous to those obtained by distillation, but it would be much more rapid, and could further be applied to bodies such as wax or paraffin, or even to explosive substances. The apparatus required would oniy be a reservoir of compressed gas and a few tubes of thick glass or metal furnished with taps.

This method of distillation is not only applicable to laboratory experiments. Compressed gas is now an article of commerce, and apparatus capable of withstanding pressures of several hundreds of atmospheres is easily obtained. There should, therefore, be no difficulty in adding compressed gas to the list of solvents employed in industrial chemistry.—*Revue Générale des Sciences*, No. 21, Nov. 15, 1898.

ELECTROLYTIC DETERMINATION OF TIN IN TIN ORES.*

By E. D. CAMPBELL and E. C. CHAMPION.

In the methods at present in use for the determination of tin in tin ores, the decomposition is effected by fusion with sodium carbonate and sulphur, in order to form sodium sulphostannate, from which the tin is obtained either by precipitation as sulphide with subsequent ignition to the oxide, or by electrolytic deposition from the ammonium sulphide or oxalate solution. Some of the objections to the Rose method of precipitation as stannic sulphide and subsequent weighing as stannic oxide are the difficulties of washing the sulphide free from sodium salts, the ignition to stannic oxide without loss of stannic sulphide, and the contamination of stannic oxide with silica.

Electrolytic deposition of tin from the ammonium sulphide solution does not seem to give entirely satisfactory results, for although the tin may be completely precipitated, it is very difficult to obtain complete deposition without at the same time precipitating some sulphur. On the other hand, under proper conditions, tin may be very satisfactorily deposited electrolytically from the double oxalate solution; and in the method herewith proposed, the principal modification is in the method of converting the tin from the sulphostannate into the double oxalate. In the method as given by Classen for the conversion of sodium sulphostannate into the double ammonium oxalate, the solution of the sulphostannate is first acidified with sulphuric acid, and the tin then oxidised to metastannic acid by means of hydrogen peroxide. The metastannic acid so formed has to be filtered, washed, and dissolved by means of ammonium acid oxalate and oxalic acid, in order to convert it into the double oxalate ready for electrolysis. It was in order to avoid any necessity of precipitating the tin and filtering it out, after it had been once obtained in solution as sodium sulphostannate, that the method given below was perfected. The method in detail, which has given us very satisfactory results on ores tested, is as follows:—

Mix one grm. of finely ground ore intimately with five to six grms. of a fusing mixture made up of equal weights of dry sodium carbonate and sulphur. Place the ore so mixed in a covered porcelain crucible, which in turn should be in a larger covered porcelain crucible. This arrangement of double crucibles will prevent oxidation of stannic sulphide during the ignition. Place the crucible upon a triangle, and cover with a large Hessian or clay crucible, from which the bottom has been removed, in such a way that the heat from the burner used in the ignition will be kept in, so that the whole of the porcelain crucible will be evenly heated. Raise the temperature of the porcelain crucibles by means of a good burner, such as the Detroit or Fletcher style, to a full red heat, and maintain the temperature for one hour. After allowing it to cool, place the inner crucible in a beaker or casserole, and dissolve out the sodium sulphostannate by heating with 40 or 50 c.c. of water. After complete disintegration of the fused mass, remove the porcelain crucible from the solution, and filter out the insoluble oxides and sulphides from the solution, which will contain almost all the tin as sodium sulphostannate. Wash the insoluble residue with hot water. This insoluble residue will usually carry a small amount of tin, and must therefore be ignited in the crucible in which the fusion was performed, and after ignition be re-fused, as in the first case, with fresh sodium carbonate and sulphur. After fusing the insoluble residue from the first fusion and dissolving out the tin, unite the solutions of sodium sulphostannate. Add to the united solutions of sodium sulphostannate hydrochloric acid, until the solution is slightly acid and the tin has been precipitated as stannic sulphide. Boil down rapidly, until the excess of hydrogen sulphide has been boiled off and the bulk of the solution has been reduced to 75 or 80 c.c. Add to the hot solution 10 c.c. of hydrochloric acid (sp. gr. 1.20). Then stir in, a little at a time, sodium peroxide, until the stannic sulphide has been completely oxidised to stannic chloride, and the solution has become clear, except for a little sulphur which collects easily on boiling for two or three minutes, and can be easily removed by filtering.

The oxidation of stannic sulphide to stannic chloride is very easily effected, requiring usually from 2 to 3 grms. of sodium peroxide. After oxidising the stannic sulphide to stannic chloride, boil two or three minutes until the separated sulphur is collected, then filter into a large platinum dish, and wash thoroughly with a little hot water. Add to the solution ammonia until a slight permanent precipitate is obtained, then 50 c.c. of a 10 per cent solution of acid ammonium oxalate. This will give a clear solution from which the tin is easily deposited.

Electrolyse over night with a current N. $D._{100} = 0.10$ ampere, with an electromotive force of 4 volts. This current can be obtained from two storage cells using suitable resistance. In the morning the tin will be found to be completely precipitated as a pure white, firmly adherent metal upon the platinum dish. When 8 volts E.M.F. were used the deposit was found to be more strongly crystalline and less firmly adherent than when lower voltage was employed. When the tin is completely deposited, disconnect and wash the tin first with water, then with alcohol. Drain off the latter as completely as possible, and dry between 80° and 90° C. If the deposited tin is found to have small crystals of ammonium oxalate adhering to it, they may be easily removed by washing with a little warm water before the final washing with alcohol. After weighing the platinum dish containing the precipitated tin, the latter is dissolved off by heating with a little hydrochloric acid, and the weight of the platinum dish obtained after washing and drying as before.

In electrolytic determination of metal where they are deposited in platinum dishes, the results will be found to be much more satisfactory if duplicate determinations are made in platinum dishes of practically the same size, and the dishes are washed, dried, cooled, and weighed under

* Contribution from the Laboratory of Analytical Chemistry, University of Michigan. From the *Journal of the American Chemical Society*, xx., No 9, September, 1898.

the same conditions, each dish serving as a counterpoise for the other. By using dishes in this way, variations of weight due to atmospheric changes may be reduced to a minimum, and the results made more accurate than when a dish is weighed alone.

LUBRICANTS FOR GLASS STOP-COCKS.

By FRANCIS C. PHILLIPS.

The success of modern chemical research work depends frequently upon the maintenance in position for considerable periods of complex forms of apparatus in which glass stop-cocks play an important part, and the failure or breakage of a stop-cock often proves to be the cause of serious loss of time or material. The efficiency of a stop-cock is, however, quite as much dependent upon the lubricant used for its protection as upon the skilful workmanship of the glass-blower in its manufacture.

It has been the common practice to employ an animal fat or a mixture of such fats for lubricating the stop-cock plugs of apparatus of all kinds and for work of every description, although it is a fact of experience that such lubricants are often a source of inconvenience and even danger to the apparatus.

A stop-cock lubricant should, besides overcoming friction, satisfy the following requirements:—

1. It should adhere to the glass, and should not be loosened by water.
2. It should be little affected by changes of temperature.
3. It should not be saponified by alkali.
4. It should be sufficiently transparent or translucent to render visible any clogging of the hole in the stop-cock plug while in use, and to show whether air spaces occur between the plug and the walls of the stop-cock.

Ordinary fats are so easily saponified and adhere so feebly to glass that they are seldom suited to the purpose. Pure rubber heated to a temperature sufficient to render it permanently viscid has advantages over fats, but its adhesiveness is lessened by moisture, and it is completely removed by alkali.

Schmitz (*Ztschr. Anal. Chem.*, 1884, 516) recommends for glass stop-cocks the use of gutta percha dissolved in a high-boiling mineral oil. This mixture, although not saponifiable, does not adhere well to glass. If thinned down sufficiently with oil, its lubricating qualities suffer, while the gutta percha tends to become granular if the mixture is made thicker.

Vaseline, which is sometimes recommended for use alone, does not adhere to the glass, and does not overcome friction.

With a view to producing a lubricant better adapted to use on glass stop-cocks, a series of experiments has been tried. Various mixtures of softened rubber with other substances were tested. On mixing together

Pure rubber	70 parts.
Spermaceti	25 ,,
Vaseline	5 ,,

a mass is obtained which lubricates well, is translucent, adheres to the glass, and is not saponifiable. The vaseline was added to the mixture to increase its softness. The materials were thoroughly mixed while hot, the rubber being melted first, and the others stirred in. It is well to use a little more vaseline in winter than summer.

Another preparation, which gave still better results, was made by mixing

Pure rubber	70 parts.
Yellow unbleached beeswax ..	30 ,,

The rubber should be pure and fresh. Old rubber, or scraps of worn out tubing, whether black or red, will not answer as well, and may cause the mixture to become more or less granular and opaque when used in the stop-cocks. The rubber is best heated in a covered vessel until thoroughly melted, and then the wax should be added. The hot mixture is well stirred. No vaseline is needed. This lubricant is very serviceable, protects stop-cocks from sticking, even when used for concentrated solutions of caustic alkalies, and is quite translucent in thin layers. Care should be used not to scorch the mixture in its preparation. Strong alkalies tend in time to loosen and emulsify all lubricants, and the stop-cocks should occasionally be cleaned and re-coated.

It has been attempted to increase the adhesiveness of such lubricants by the addition of small quantities of balsam of fir and other strongly adhesive substances, but difficulty was found from the tendency to cause sticking of the stop cock plug. The rubber mixtures should not be exposed to the air longer than is necessary during the heating, and they should be preserved in closed bottles.

Various mixtures of gutta percha with wax and with oils were tried, but the gutta percha tends to cause granulation and diminishes adhesiveness. The mixtures above recommended may be readily removed from parts of glass apparatus, which are difficult of access for cleaning, by the use of a little concentrated nitric acid, which quickly attacks and loosens it so that it may be washed out by water.

No lubricant is fit for use unless it renders the stop-cock nearly or quite translucent, so as to show whether or not the plug is coated over its entire length.

A thick rubber and wax mixture is especially suited for well-ground glass stop-cocks upon gas vessels which are to be exhausted, and which have therefore to sustain the full pressure of the atmosphere. Such mixtures have been in use for stop-cocks of ordinary burettes in volumetric work during about two years, and have given satisfactory results in every way.—*Journal of the American Chemical Society*, xx., No. 9.

THE ALKALINE REACTION OF SOME NATURAL SILICATES.*

By F. W. CLARKE.

That pure water exerts a distinct solvent action upon many natural silicates has long been known. As far back as 1848 the Rogers Brothers published a series of observations upon this subject, (*Am. Journ. Sci.*, vol. v., No. 2, 401), and showed that some species of minerals would give an alkaline reaction to test paper. They did not, however, give details concerning the individual minerals thus investigated. The more recent researches of Daubrée and of Cossa are well known.

By the use of phenolphthalein as an indicator the alkalinity of many silicates can be demonstrated with the utmost ease, and the experiments described below serve to bring out very clearly the relative decomposability of certain minerals and rocks by pure water. The method adopted was as follows: A series of glass-stoppered bottles was placed against a white background. In each bottle half a grm. of finely pulverised mineral was put, and then 50 c.c. of distilled water, containing a very little alcoholic phenolphthalein, was added. As the indicator was mixed, once for all, with the total amount of water taken for the entire series, the 22 samples examined were treated exactly alike. Two of the bottles were filled with the water and indicator in blank, in order that possible action upon the glass itself might be detected if it occurred. The two blanks, however, remained colourless

* Read at the Boston meeting of the American Chemical Society, August, 1898. From the *Journal of the American Chemical Society*, vol. xx., No. 10.

during the two weeks through which the experiments lasted. The results obtained were as follows:—

Muscovite.—A doubtful trace of colouration, which soon disappeared.

Lepidolite.—Like muscovite.

Phlogopite.—The peculiar non fluoriferous variety from Edwards, N.Y. Gave a very distinct, permanent, pink colouration.

Orthoclase.—A trace of colouration which increased for a few days and then faded.

Oligoclase.—The transparent variety from Bakersville, N.C. Distinct and permanent, but pale colouration.

Albite.—From Amelia County, Va. Gave a good, permanent, alkaline reaction.

Leucite.—A slight reaction at first, which faded in a few days.

Nephelite.—The elæolite from Litchfield, Maine. Good colouration, but partly fading in time.

Cancrinite.—Litchfield, Maine. Gives a deep rose colouration, which is permanent.

Sodalite.—From Canada. A deep, permanent rose colour.

Spodumene.—The transparent, yellow variety from Brazil. A good reaction, but gradually fading.

Scapolite.—The wernerite from St. Lawrence County, N.Y. Gave a faint, evanescent trace of colouration.

Laumontite.—A doubtful trace of colouration.

Stilbite.—Faint, evanescent colouration.

Chabazite.—Like stilbite.

Heulandite.—Slight reaction, but distinct.

Thomsonite.—Variety lintonite. A fairly strong reaction, fading in time,

Analcite.—Good alkaline reaction.

Natrolite.—From Bohemia. Strong colouration, permanent.

Pectolite.—From Bergen Hill. Gave a very deep rose colour.

Apophyllite.—From Bergen Hill. A very deep rose colour.

In nearly every case the reaction was obtained at once, showing a more rapid action of water upon the silicate than had been anticipated. In some instances fading is noted. This is doubtless due, in general, to the action of light; but in certain cases the coloured solution separated into two layers, the colour being wholly in the lower. Here the colour was really held as a coating upon the fine solid particles, and as they subsided the appearance of stratification was produced. Towards the end of the experiments the mineral aegirite was added to the series. This also gave a strong alkaline reaction and a fairly deep rose colour.

A neat method of demonstrating the reactions described above is the following:—Place a little of the mineral to be tested in a watch-glass upon a sheet of white paper. Add a drop of alcoholic phenolphthalein solution, and then a few drops of pure water; in most cases the reaction is given instantaneously. Orothoclase gave no colouration, leucite a trace, and scapolite a trace; albite, nephelite, and phlogopite furnished distinct reactions. Under the same circumstances thomsonite, aegirite, natrolite, cancrinite, sodalite, pectolite, and apophyllite gave immediately a deep rich rose colour. The strongest alkaline reactions seemed to be given by pectolite and apophyllite.

In general, the order of intensity of the colour produced was what might have been expected. Among the micas, muscovite and lepidolite showed little or no solubility, while phlogopite was distinctly attacked. In nature the magnesian micas are far more easily alterable than muscovite, a fact which is reiterated by these experiments. Again, orthoclase was slightly dissolved, albite much more so, and oligoclase gave a reaction between the two; that is, more than the one, less than the other. In other words, the plagioclase felspars alter more easily than orthoclase, as is apparent in the study of the rocks themselves.

In order to bring out the latter point more clearly, a series of rocks which had been analysed in the laboratory of the U.S. Geological Survey, was placed in a row of bottles, and treated just as the mineral species had been, with water and phenolphthalein. A granite and an amphibole gabbro gave no alkaline reaction. A rhyolite, trachyte, leucite basalt, felspar basalt, and diorite gave faint traces of colour. Granitite, gneiss, phonolite, diabase, and camptonite yielded distinct alkaline colourations.

In all of these instances the production of colour is doubtless due to the solution from the mineral or rock of alkaline silicates. The noteworthy point is the quickness with which the reaction can be obtained. With minerals like cancrinite, sodalite, natrolite, pectolite, and apophyllite the reaction is striking enough to be used as a lecture-table experiment.

THE GASES OF THE ATMOSPHERE.

BERLIN, *Dec.* 19.

PROFESSOR WILLIAM RAMSAY this evening delivered a lecture by special invitation to the members of the Berlin Chemical Society in the Chemisches Institut. Professor Liebermann presided and welcomed his distinguished English colleague in words conveying the most cordial recognition of his achievements. There was a crowded audience, among whom were Professor Virchow, Professor Liebreich, Professor von Bezold, Professor Warburgh, Professor Fischer, and, in fact, every chemist of eminence in Berlin.

Professor Ramsay had chosen for his subject "The New Gases and their Relations to the Periodic Law." He gave a most interesting account of the various properties of helion, argon, metargon, neon, and xenon, and illustrated his more recent investigations by limelight views of the appliances of his laboratory and by the spectra of the various gases, most of those present following his explanations with the aid of pocket spectroscopes. The lecture, which was very fluently delivered in German, paid warm tribute to the work of Lord Rayleigh and to the assistance rendered to Professor Ramsay in the course of his experiments by Dr. Travers and others. At its close, amid loud cheers, Professor Liebermann thanked the distinguished lecturer for having devoted a portion of his vacation to the instruction of his Berlin colleagues and admirers, and described him as having by his indomitable energy and perseverance united the realms of physics and of chemistry.

BERLIN, *Dec.* 20.

The Emperor and Empress this afternoon were present at a lecture and demonstration by Professor Ramsay dealing with the recently discovered gases. The lecture was delivered at the Chemisches Institut in Berlin, by special desire of her Majesty, and was, therefore, of a semi-private character. Their Majesties, accompanied by the British Ambassador, Sir Frank Lascelles, whom the Emperor had graciously invited to be present, occupied chairs in front of the auditorium. Professor Ramsay spoke in English for about half-an-hour, and illustrated his account of the new gases by limelight views and by Geissler tubes for exhibiting the spectral analysis of the gases. At the close of the lecture, the Emperor and Empress conversed for some time with Professor Ramsay.

Professor Ramsay was last night the guest of the Berlin Chemical Society at supper in the Savoy Hotel. To-morrow he will comply with a request which has been made to him to deliver a lecture in the Urania, the Berlin popular institute of astronomy and other sciences.—*The Times*, December 20 and 21.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 17th, 1898.

Professor DEWAR, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. William Harcourt Branscombe, Verona, Eastbourne; Harry Estcourt Estcourt, Hayesleigh, Old Trafford, Manchester; George Cecil Fry, 1, Edinburgh Terrace, Newbury, Berks; John Golding, 1, Balmoral Road, Nottingham; Henry Winstone Harper, M.D., Austin, Texas, U.S.A.; James Hembrough, 159, Hotwell Road, Clifton, Bristol; Alfred Lucas, Maison Hussein Pasha, Cairo, Egypt; Samuel Montagu Martin, Westwood, Princetown Road, Bangor, co. Down; James Henry Pizey, 9, Lady Somerset Road, Highgate Road, N.W.; Robert Coleman Price, Blacksburg, Virginia, U.S.A.; Frederick Soddy, Merton College, Oxford; Louis Heathcote Walter, 83, Holland Park Avenue, W.; William Arthur Williams, 75, High Street, Wapping, E.

The following candidates are recommended by the Council, under Bye-law I. (3):—Charles Robert Carroll, Hyderabad, Deccan, India; William Lash Miller, B.A., Ph.D., the University of Toronto; Frederick Louis Wilder, Villa Nova de Lima, Minas Geraes, Brazil.

The following papers were read:—

133. "*Determination of the Constitution of Fatty Acids.*" Part I. By ARTHUR W. CROSSLEY and HENRY R. LE SUEUR.

The paper gives a detailed account of experiments undertaken with the idea of devising a method for the determination of the constitution of fatty acids. An acid, $CH_2X{\cdot}CH_2{\cdot}CO_2H$, is first converted into the ethylic salt of the monobromo-derivative, $CH_2X{\cdot}CHBr{\cdot}CO_2Et$, which is then treated with quinoline or diethylaniline, whereby the elements of hydrogen bromide are removed, and the ethylic salt of an unsaturated acid of the acrylic series, $CHX{:}CH{\cdot}CO_2Et$, is produced. The acid obtained by hydrolysing this salt is oxidised with potassium permanganate, giving rise to the corresponding dihydroxyacid, $CHXOH{\cdot}CHOH{\cdot}CO_2H$, which is then oxidised with chromic acid, with the production of the acids $X{\cdot}CO_2H$ and $CO_2H{\cdot}CO_2H$. A fatty acid (or ketone) containing two carbon atoms less than the original acid has thus to be identified, and as the number of isomerides decreases greatly with loss of two carbon atoms, the possibility of identification is much enhanced.

The method has been carried out with valeric, isovaleric, and isobutylacetic acids with good results, the products identified being propionic acid, acetone, and isobutyric acid respectively.

The authors propose to continue the investigation with higher fatty acids, such as ethylisopropylacetic and stearic acids, and with a dibasic acid, such as pimelic (isopropylsuccinic) acid.

134. "*The Crystalline Form of Iodoform.*" By WILLIAM JACKSON POPE.

Considerable difficulty is experienced in obtaining iodoform in well developed crystals from solutions in the ordinary organic solvents, but it separates from acetone in magnificent six-sided tablets belonging to the hexagonal system. The crystals exhibit the forms $c\{111\}$, $r\{100, 22\bar{1}\}$, $p\{\bar{1}10\}$, and $m\{2\bar{1}\bar{1}\}$, and have the axial angle $\alpha = 93° 41'$; the double refraction is negative in sign and strong.

135. "*The Characterisation of Racemic Compounds.*" By FREDERIC STANLEY KIPPING and WILLIAM JACKSON POPE.

Having previously shown that crystallographic data afford a sure basis for the characterisation of racemic compounds, the authors now give the results of their examination of a method suggested and made use of by Ladenburg for this particular purpose.

Ladenburg stated (*Ber.*, 1894, 27, 3065) that if, on fractionally crystallising a mixture of an externally compensated substance with excess of one of the active constituents, the various fractions differ in specific rotation, the existence of a racemic compound is established; if, on the other hand, the various fractions have the same specific rotation, then the existence of a racemic compound is disproved.

The authors point out that the argument upon which Ladenburg's method is based is fallacious, and, further, on examining experimentally several cases of mixtures of an externally compensated substance with an excess of one of the optically active isomerides, they find that the method is valueless.

Mixtures of the non-racemic inactive sodium ammonium tartrate with the isomeric dextrotartrate, and of the racemic inactive sodium potassium tartrate with the corresponding dextrotartrate, were fractionally crystallised, and it was found that in each case the excess of dextrorotatory salt separated out first, most of the externally compensated substances remaining in the mother liquors.

136. "*The Occurrence of Orthohydroxyacetophenone in Chione Glabra.*" By WYNDHAM R. DUNSTAN and T. A. HENRY.

The wood of *Chione glabra*, a large flowering tree indigenous to Grenada, has a strong aromatic, somewhat fœcal, odour. This is due to a volatile oil which the authors find is chiefly composed of *orthohydroxyacetophenone*, $C_6H_4Ac{\cdot}OH$. The oil also contains a minute amount of what appears to be the crystalline methyl ether of this substance, $C_6H_4Ac{\cdot}OMe$.

The properties of orthohydroxyacetophenone, prepared in the laboratory from orthonitrocinnamic acid as a starting point, agree precisely with those of the volatile oil of *Chione glabra*.

DISCUSSION.

In reply to Dr. Harden, Professor DUNSTAN said that he thought the degradation of vegetable proteid a possible mode of origin of indole derivatives, though some botanists were of opinion that it was more probable that they resulted from simpler synthetic processes.

137. "*Preparation of Hyponitrite from Nitrite through Oxyamidosulphonate.*" By E. DIVERS and T. HAGA.

The authors have already published, disconnectedly, the facts (1) that sodium nitrite can be very completely and easily changed into oximidosulphonate by dissolving it with the calculated quantity of sodium carbonate, and passing sulphur dioxide into the solution; (2) that sodium oximidosulphonate can be hydrolysed very exactly into oxyamidosulphonate; and (3) that sodium oxyamidosulphonate can be largely decomposed into hyponitrite and sulphite by dissolving much potassium hydroxide in its concentrated solution. Details are now given by which, taking advantage of these facts, sodium nitrite can be converted into 60 per cent of its equivalent of silver hyponitrite. The essential points are to keep the temperature at 0° during the sulphonation of the nitrite; to allow the oximidosulphonate to hydrolyse, in the absence of sulphite, at or near the common temperature, during about 24 hours, so as to produce only oxyamidosulphonate and acid sulphate; to neutralise the solution by alkali carbonate, then dissolve in it sufficient potassium hydroxide to make the solution one of about equal weights of the hydroxide and water (having taken care from the first to use as little water as possible), and allow the whole to stand during 30 hours; to fractionally precipitate the hyponitrite by silver sulphate (or nitrate) from the greatly diluted alkaline solution, leaving the sulphite and the alkali in solution; to separate the silver hyponitrite from the metallic silver, &c., which accompanies it, by dissolving it in very cold dilute sulphuric acid, then

filtering, and finally neutralising the sulphuric acid by sodium carbonate with the greatest expedition. Some oxyamidosulphonate always escapes decomposition by the potassium hydroxide; of that decomposed about 80 per cent becomes hyponitrite, and the rest nitrous oxide and alkali, besides, of course, sodium sulphite in either case.

138. "*Absorption of Nitric Oxide in Gas Analysis.*" By E. DIVERS.

A concentrated alkaline solution of sodium or potassium sulphite absorbs nitric oxide completely and quickly, forming with it alkali (hypo)nitrososulphate, and can be used in gas analysis with satisfactory results.

139. "*Interaction of Nitric Oxide with Silver Nitrate.*" By E. DIVERS.

Silver nitrate decomposes freely in a current of nitric oxide at much lower temperatures than when heated in air or carbon dioxide. The products, apart from oxygen, are the same, namely, nitric peroxide, silver, and silver nitrite, except that the silver nitrite is, for a time, an abundant product in presence of nitric oxide, whereas in its absence, when the temperature of decomposition is much higher, only a little of the nitrite is ever found, because it passes probably into nitric peroxide and silver nearly as fast as it is produced.

Either nitric oxide acts directly upon the silver nitrate, or, what is more probable, the imperceptible decomposition of silver nitrate alone, at temperatures of 220—250°, into oxygen and nitrite becomes rapid and marked in presence of nitric oxide, in consequence of the latter taking up oxygen as fast as it is formed by the decomposing nitrate.

Nitric oxide has no effect on heated sodium, potassium, barium, and lead nitrates.

140. "*Preparation of Pure Alkali Nitrites.*" By E. DIVERS.

Alkali nitrites are easily obtained pure and in concentrated solution by passing nitrous gases containing slight excess of nitric oxide into concentrated solutions of pure potassium or sodium hydroxide or carbonate, out of contact with air. With ordinary care no nitrate is formed; it is a current mistake to suppose that it is.

Both nitrites are slightly yellow, and their concentrated solutions markedly yellow. The sodium salt melts at 213°; at 15°, six parts of water dissolve five parts of it. Its crystals are often very large, but very thin, flattened prisms, moderately deliquescent. Sodium nitrite can be readily purified by re-crystallisation; potassium nitrite cannot. Potassium nitrite occurs only in minute, short prisms, and is soluble in one-third of its weight of water. It is exceedingly deliquescent, but its crystals are actually anhydrous, although Lang and Hampe independently found them to contain $\frac{1}{2}H_2O$.

DISCUSSION.

Mr. GROVES remarked that sodium nitrite is manufactured on a large scale for use in the colour industry, and is sent into the market nearly pure, containing some 98 per cent of the salt, but as far as his experience went neither the salt nor the solution is yellow.

He had found that when arsenious anhydride is heated at 70° with nitric acid of sp. gr. 1·3, nearly pure nitrous anhydride, mixed only with a little nitric oxide, is evolved, and that a dilute solution of nitrous acid could readily be prepared by passing this vapour into water at 0° containing some crushed ice.

141. "*The Reduction of an Alkali Nitrite by an Alkali Metal.*" By E. DIVERS.

Nitrous oxide, nitrogen, hydroxylamine, ammonia, sodium hyponitrite, and sodium hydroxide are invariably products of the reduction of sodium nitrite by sodium amalgam, but the process can be modified so that each of them in turn shall be formed in any desired quantity between a very small amount and a certain maximum. The principal points needing attention are the degree of concentration of the solution and the temperature at which the reduction takes place.

The quantity of hyponitrite will be equivalent to more than one-sixth of the nitrite when the solution is concentrated and is not allowed to grow too hot; by large dilution, alone or aided by heat, it can be made indefinitely small. That of hydroxylamine may be made to be anything between one-eleventh and one three-hundredth of the equivalent of the nitrite, sufficient dilution and cooling being the conditions for a high yield of hydroxylamine. Ammonia being merely reduced hydroxylamine, its yield depends on that of hydroxylamine and reduction of this by the further action of the amalgam. The temperature at which the reduction is allowed to proceed determines how much of the gaseous products shall be nitrous oxide and how much nitrogen, high temperature causing the production of nitrogen. The two gases together are always nearly equivalent to a little more than four-fifths of the nitrite.

Sodium amalgam is entirely without action upon sodium hyponitrite. It has always very little action, if any, upon nitrous oxide at the common temperature. Sodium hyponitrite in concentrated sodium hydroxide solution is very stable and may be heated at 100° without effervescing. During the reduction of the nitrite, the gases produced may be seen to come exclusively from the surface of the solution touching the amalgam. As already indicated, the production of nitrous oxide and of nitrogen is at the expense one of the other, not at that of the hyponitrite or hydroxylamine. Similarly, the hyponitrite and hydroxylamine increase each at the expense of the other. Yet it does not seem that the nitrogen is produced by reduction of the nitrous oxide, and certainly the hydroxylamine is not a reduction product of the hyponitrite. It also does not seem that the nitrous oxide comes from the decomposition of the sodium hyponitrite to any important extent.

Sodium nitrite, reduced by sodium amalgam, passes, it would seem, first into the unknown transition products, NaNO and NaON, to the extent of four-fifths into the former and one-fifth into the latter. From the latter, or sodioximide radicle, the hyponitrite will be formed by condensation when the alkali solution is concentrated, and the hydroxylamine by reduction when the alkaline solution is dilute. From the former, or sodium nitroside radicle, the nitrous oxide will be produced by condensation and hydrolysis at low temperatures, or the nitrogen by reduction, condensation, and hydrolysis, at high temperatures.

The reduction of potassium nitrite by potassium amalgam proceeds closely on the same lines as that of sodium nitrite by sodium amalgam.

142. "*Hyponitrites; their Preparation by Sodium or Potassium and Properties.*" By E. DIVERS.

Sodium nitrite reduced in concentrated solution by sodium amalgam, yields a third of its weight of silver hyponitrite, and nearly the equivalent amount of several other hyponitrites, without the need of this salt as an intermediary. In this respect, the process has an advantage over the oxyamidosulphonate method. The hydroxylamine, which always accompanies the sodium hyponitrite, is easily got rid of by the continued action of the sodium amalgam, which is without action on the hyponitrite itself. The resulting ammonia is removed by exposure of the solution over sulphuric acid for a night under reduced pressure. Mercuric oxide, employed by all other chemists to remove hydroxylamine, has the fault of regenerating nitrite. The concentrated solution of sodium hyponitrite and hydroxide, thus obtained, is remarkably stable. In the preparation from it of other salts than the sodium salt itself and the silver salt, the sodium hydroxide has first to be neutralised, after diluting the solution with ice and water, mercurous nitrate being employed as an indicator with portions of the solution.

Sodium hyponitrite is prepared from the most con-

centrated alkaline solution, obtained as above, by precipitation with absolute alcohol, or (Jackson) by evaporation in a vacuum and washing the salt with alcohol. It forms minute, crystalline granules, $(NaON)_2+5H_2O$, which effloresce and evolve nitrous oxide in the air, but in a vacuum desiccator are converted into an anhydrous non-coherent powder, stable in dry air. The anhydrous salt bears a somewhat high temperature in dry air without decomposition, then fuses and effervesces, forming sodium oxide, sodium nitrite, and nitrogen. According to Prof. Ikeda, sodium hyponitrite gives numbers for its molecular magnitude approximating to those required for $(NaON)_2$ by Lowenherz's cryoscopic method.

Silver hyponitrite is prepared by adding a highly dilute solution of silver sulphate or nitrate to the alkaline solution already described. It decomposes exceedingly slowly in the most state, forming products similar to those obtained on heating. It is also decomposed by bright light, becoming brown, but is not blackened, by the light alone. When heated, it is decomposed without explosion, its yellow colour changing directly to that of metallic silver, without intermediate darkening; the products are silver, silver nitrate, nitrogen, nitric oxide, and nitric peroxide. A study of the change renders it most probable that the nitric oxide and silver nitrate are not primary products, but arise from interaction between the nitric peroxide and undecomposed hyponitrite. Sodium chloride solution digested with excess of silver hyponitrite has only 25/43 of its chlorine displaced by the hyponitrite ion. Paal's supposed silver nitrito-hyponitrite, $Ag_2N_2O_3$, appears not to exist.

The preparation and properties of mercuric, mercurous, cupric, lead, barium, strontium, calcium, and potassium hyponitrites are described. Cuprous hyponitrite could not be obtained, nor were Rây's basic mercuric compounds met with. Maquenne's hypo-isonitroso-acetates were examined, and the formula—

$$OAc{\cdot}Ca{\cdot}O{\cdot}N_2{\cdot}OAc,Ca(OAc)_2,5H_2O$$

is suggested for the calcium salt.

Hyponitrous acid, in solution, is more acid to litmus paper than carbonic acid, but its effect disappears as the paper dries. It decomposes slowly into nitrous oxide and water (and nothing else except a trace of nitrous acid having another origin). When pure, it has no action on iodine-water or with the starch-iodide test. It decomposes silver carbonate, sulphate, nitrate, and chloride, when present in excess, but not the iodide. It is easily oxidised, but is unaffected by reducing agents. Apparently it has not yet been obtained free from every trace of nitrous acid; when carefully prepared, it will remain, however, for more than an hour without producing a blue colour with the starch-iodide test. Hyponitrous acid can be estimated gravimetrically as the silver salt, and volumetrically by potassium permanganate. Thum's permanganate process, in which the hyponitrous acid becomes ultimately nitric acid, is an excellent one; the failure of Hantzsch and Sauer and of Kirschner in its use is due to the modifications they made in it.

Discussion.

Professor DUNSTAN remarked that Dr. Divers in the present series of papers had cleared up a number of doubtful points. In connection with the formation of hyponitrite by the reduction of nitrite in aqueous solution, Dr. Divers had confirmed the observations made in 1887 by Mr. Dymond and himself, as to the simultaneous production of hydroxylamine and its non-formation by the further reduction of hyponitrite. He still adhered to the view that they put forward that these results were best explained by the assumption that the nitrite was first hydrogenated, forming a compound of the formula $NaN(OH)_2$, which on the one hand loses water, forming hyponitrite, and on the other is hydrolysed, forming sodium hydroxide and dihydroxylamine, $NH(OH)_2$, which by further reduction furnishes hydroxylamine.

Mr. G. N. HUNTLY pointed out that the hypothesis of the formation of dihydroxylamine, as a first reduction product, suggested by Professor Dunstan, had the advantage of being equally applicable to the two other methods of preparing hyponitrites, viz., from sodium hydroxylaminesulphonate (Divers) and benzenesulphohydroxamic acid (Piloty), by the action of concentrated potash. The three reactions on this hypothesis would be represented as follows:—

1. $NH(OH)(SO_3Na+KOH=KNa{\cdot}SO_3+NH(OH)_2$;
2. $NH(OH)(SO_2{\cdot}C_6H_5)+KOH=C_6H_5{\cdot}SO_2K+NH(OH)_2$;
3. $HO{\cdot}NO+2H=NH(OH)_2$.

In alkaline solution, the dihydroxylamine would condense thus—

$$OH{\cdot}NH{\cdot}OH+H(OH)N{\cdot}OH=OH{\cdot}N{:}N{\cdot}OH+H_2O,$$

and there being no tendency to condensation in acid solution, further reduction should give hydroxylamine, a conclusion in accordance with the facts observed by Professor Divers.

143. "*Paranitro-orthanisidine.*" By RAPHAEL MELDOLA, F.R.S.

As paranitro-orthanisidine (m. p. 139—140°), which was described in a paper published in conjunction with Messrs. Woolcott and Wray (*Trans.*, 1896, vol. lxix., 1330), has recently been made the subject of a patent by the Fabriques de Produits Chimiques de Thann et de Mulhouse (Germ. Pat., 98637 of 1897), the author records some further observations which have been made with the substance, as it is proposed to continue its investigation.

The acetyl derivative, purified by repeated crystallisation from water so as to get rid of the isomeric metanitro-derivative simultaneously formed, melts at 153—154°, the melting point 143—146° given in the former paper being that of the mixed isomerides. The acetyl-derivative of *p*-nitro-*o*-anisidine can be reduced by dissolving in hot water and agitating with iron dust and a little acetic acid. The *p*-amido-*o* acetanisidide thus formed is somewhat unstable, and has not yet been isolated. It is readily diazotisable, and the NH_2-group has by this means been replaced by iodine with the formation of *p-iodo-o-acetanisidide*, [NHAc : OMe : I = 1 : 2 : 4]. This compound crystallises in beautiful silvery scales melting at 175—176°.

0·1778 gave 74 c.c. moist nitrogen at 19° and 764 mm. N = 4·80.

0·202 gave 0·1618 AgI. I = 43·28.

The formula requires N = 4·81 per cent; I = 43·64 per cent.

Mr. Frederick Henry Streatfeild was assisting in this investigation, but having left to accept an appointment elsewhere, the work was temporarily interrupted.

NOTICES OF BOOKS.

Government Agricultural Experimental Station for North Dakota. — Bulletin No. 32. Fargo, North Dakota. 1898.

THIS Bulletin deals with five subjects, viz., drinking water, wool scouring, soil humus, analysis of foods, and vinegar. With regard to the water question, the permissible amount of total solids is here discussed; a considerable difference of opinion is shown by different authorities,—one puts the amount permissible at 57·5 parts per 100,000, another says the safe limit is only 30 parts, but that 100 parts should condemn the water.

A number of supplies to large cities in the United States show a variation between 4·7 and 34 parts per 100,000, but too much weight should not be given to such figures, as the composition of the dissolved matter must most materially influence its power for good or evil, this again depending to some extent on the constitution of the individual. A further list of twenty water supplies is also given, all of which contain considerable amounts of

sulphate of sodium (Glauber's salts); the continued use of such waters cannot but be considered as harmful.

The subject of humus in soils is also carefully considered, and some very interesting data are given, the summary of results showing that continuous wheat growing seriously impoverishes the soil; as much as five pounds of organic matter is lost for every pound which goes to furnish nitrogen for the wheat. By the loss of humus the soil becomes less retentive of moisture, and gives it up much more readily by evaporation; burning the stubble again destroys much organic matter and humates. The best way to keep up the supply of humus in the soil is to imitate Nature, and, for the present, grow at least one crop in five of grass; clover would be an ideal crop to maintain the supply of humus, and also to aid in collecting nitrogen from the air, but any grass will serve to supply humus.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 13, September 26, 1898.

Action of Lime and Calcium Carbonate on certain Natural Earthy Substances.—G. André.—The author has already indicated the possibility of determining the constitution of natural humic substances by examination of the nitrogenous products generated on treatment with potash and hydrochloric acid respectively. In the present paper a description is given of the treatment of similar specimens of earths with lime, with chalk, and with water. The results of estimation of the nitrogen in the products obtained are tabulated. It is observable that, in the case of each specimen, less nitrogen was evolved as ammonia under the influence of lime than was previously evolved under the influence of potash. The same remark applies to the amount of nitrogen found in soluble form in the lime liquor after filtration. The actions of chalk and of water give less significant results. In the case of exclusively acid soils (turf, heather-mould) it would be necessary to find another agency by which the amides of the soil may be brought into soluble form, in order to explain how this organic nitrogen changes to the ammonia which is necessary to the plants. Apparently the action of microbes alone is at work, since the presence of mineral bases cannot be taken into consideration; or the plants growing in acid soils may be capable of absorbing certain oxides directly, without transformation of the latter into ammoniacal salts.

No. 14, October 3, 1898.

Analysis of some Samples of Commercial Calcium Carbide.—Henri Moissan.—Usually calcium carbide is prepared commercially from coke, which contains large quantities of mineral matter. The chalk also which is used in its manufacture often contains silicates of aluminium, and various phosphates and sulphates. The carbide, therefore, has for impurities phosphide of calcium, sulphide of aluminium, besides various silicides,—consequently the addition of water produces, besides acetylene gas, both phosphoretted and sulphuretted hydrogen. These impurities are one of the greatest difficulties when acetylene is used for lighting purposes. Commercial carbide, of which 1 kilo. should give 349 litres of acetylene theoretically, gave, in the seven samples examined, from 292·8 to 318·7 litres. These numbers are lower still if the carbide is not crystalline, but porous and of a greyish colour. Ammonia and nitrogen were also found in the gas. In order to study the insoluble residue from the carbide, the latter was decomposed by sugar solution, so that the chalk remained in solution, and the residue could be collected. This was found to consist of carbon, calcium and iron silicides.

Preparation and Properties of Double Carbides of Iron and Chromium, and of Iron and Molybdenum.—P. Williams.—The author has prepared the two new double carbides, $3Fe_3C.2Cr_3C_2$ and $Fe_3C.Mo_2C$. These carbides, as in the case of the previously described double carbide of iron and tungsten, can be considered as compounds of carbide of iron, Fe_3C, and the metallic carbides prepared by M. Moissan in the electric furnace. It is remarkable that this double carbide of iron and chromium, $3Fe_3C.2Cr_3C_2$, enters into the same series as those compounds $3Fe_3C.Cr_3C_2$ and $Fe_3C.3Cr_3C_2$, isolated by A. Carnot and Goutal. There is always a certain relation between the carbide produced and the quantity of free graphite present. The quantity of carbide is, in some measure, inversely proportional to the quantity of free graphite. The method of cooling the crucible also influences the proportions, as has already been shown by Moissan in the production of carbide of iron in the electric furnace.

New Combinations of Phenylhydrazine with certain Metallic Salts.—M. Pastureau.—M. Schyerring, in 1893, discussed the combinations of phenylhydrazine with the sulphates of the metals of the magnesium series, and in 1897 M. Moitessier extended this study to the principal salts of this series—chlorides, bromides, iodides, acetates. The present paper describes the preparation and properties of compounds of phenylhydydrazine with bismuth chloride ($BiCl_3\,6[N_2H_3C_6H_5]$), with bismuth nitrate ($Bi(NO_3)_3 6[N_2H_3C_6H_5]$), with zinc sulphite—

$$(ZnSO_3.2[N_2H_3C_6H_5]),$$

and with manganese sulphite ($MnSO_3.2[N_2H_3C_6H_5]$).

MEETINGS FOR THE WEEK.

TUESDAY, 27th, THURSDAY, 29th, SATURDAY, 31st.—Royal Institution, 3. (Christmas Lectures). "On Astronomy," by Sir Robert Stawell Ball, F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. LXXVIII., No. 2040.

THE ORIGIN OF THE GASES EVOLVED ON HEATING MINERAL SUBSTANCES, METEORITES, &c.*

By MORRIS W. TRAVERS, D.Sc.

(Concluded from p. 307).

Meteorites.

It has long been known that considerable quantities of gas are evolved when meteorites are heated *in vacuo*. The gas usually consists of hydrogen, carbone monoxide, carbon dioxide, and hydrocarbons, in varying proportions, and attempts have been made to draw conclusion as to the origin of different meteorites from the results of analysis of the gases obtained by heating them. These speculations are based upon the supposition that the gases evolved on heating are present as such in the meteorite, occluded from the atmosphere in which it previously existed.

Beyond the gases already mentioned, the results of many observers appear to show that nitrogen is also invariably present. Among those that I have examined the gas evolved on heating contained, in no single instance, a trace of nitrogen (*Roy. Soc. Proc.*, 1897, vol. lx., p. 442). Graham (*Roy. Soc. Proc.*, 1867, vol. xv., p. 502) found as much as 10 per cent of nitrogen in the gas from the Lenarto meteorite, and Mallet (*Roy. Soc. Proc.*, 1872, vol. xx., p. 365) found 10 per cent of nitrogen in the gas from a meteorite from Augusta Co., Virginia. Wright (*Amer. Journ. Sci.*, [3], vol. ix., pp. 294 and 459; vol. x., p. 44; vol. xi., p. 254) examined a large number of meteorites, and found that in almost every case the gas contained nitrogen. In this case, however, the presence of nitrogen can easily be accounted for, as no particular precautions were taken with regard to the thorough exhaustion of the apparatus employed. A Sprengel pump was used, "which was kept running till the air was thoroughly removed, *as could be seen by the gauge.*" Dewar (*Roy. Inst. Proc.*, 1886, p. 545) found nitrogen, in quantities not exceeding 4 per cent of the total gas, in the gases from samples of meteorites and graphite.

In one single case a meteorite has been found to yield a trace of helium on heating (*Nature*, 1896).

With regard to the carbon dioxide and combustible gases, it is difficult to obtain direct evidence as to their origin. In the case of meteorites containing bituminous matter and carbonaceous nodules, the evolution of these gases may be attributed to the destructive distillation of their constituents. Meteorites of the stony variety appear to evolve more carbon dioxide and hydrocarbons, and less hydrogen and carbon monoxide, than those which are of a metallic nature. Several specimens of stony meteorites have been carefully examined by Wright and Dewar with the following results:—

Wright (*loc. cit.*) found that in the case of a stony meteorite from Iowa Co., Iowa, the carbon dioxide was given off at a very low temperature. The following table shows the composition of the gas given off at different temperatures:—

	At 100°.	At 250°.	Below red heat.	Dull red heat.	Full red heat.
CO_2	95·46	92·32	42·27	35·82	5·56
CO	0·00	1·82	5·11	0·49	0·00
H_2	4·54	5·86	48·06	58·51	87·53
N_2	0·00	0·00	4·56	5·18	6·91

* A Paper read before the Royal Society, November 24, 1898.

The meteorite lost about 10 per cent of its weight of water on heating. The water was allowed to collect in the apparatus, and as no drying reagent was used, it is easy to account for the presence of hydrogen in the gas. The carbon dioxide may have been present as an unstable hydrated carbonate, or in the state of occlusion in the pores of the substance.

Dewar (*loc. cit.*) showed that a meteorite of a similar nature was capable of re-absorbing water and carbon dioxide after the gases had been removed by heating *in vacuo*. The following results were obtained:—

	Gas in volumes of meteorite.	CO_2.	CO.	H_2.	N_2.
After 24 hours ..	0·61	54·0	—	42·4	3·6
After 6 days more..	2·47	47·0	5·0	47·0	1·0
After 8 days more..	0·63	96·1	2·0	1·5	—

The quantity of water re-absorbed after the second heating was very small, and it is interesting to note that the quantity of hydrogen evolved during the subsequent heating was also very small. From this it would appear that the hydrogen was produced directly from the water. There is no evidence to show whether the carbon dioxide entered into combination with some constituent of the meteorite or not.

Meteorites of the second class usually consist chiefly of metallic iron, nickel, &c., with small quantities of crystalline minerals, such as olivine. The presence of these minerals, which are usually hydrated silicates containing ferrous oxide, might in themselves account for the formation of hydrogen. The carbon monoxide might be produced by the interaction of carbon dioxide, the product of decomposition of a carbonate, with the metallic iron. The small quantities of hydrocarbon, which are also present in the gas, and which appear to belong to the saturated series, might be produced by the action of water, which is invariably present, upon metallic carbides. The changes which take place are probably of a complicated nature.

In order to ascertain whether a sample of meteoric iron actually contained occluded or enclosed gases, the following experiment was performed. A piece of meteoric iron was cut into fine shavings, which were carefully cleaned. The metal was divided into two portions; one part was heated in a sealed tube with copper sulphate and water, in the manner already described, the other was heated *in vacuo*. The gases evolved were in each case collected and analysed.

	By action of heat.	Copper sulphate experiment.
Hydrogen	0·322 c.c. per grm.	0·014
Carbon monoxide and hydrocarbons ..	0·164 „ „	
Carbon dioxide	2·222	0·739

The trace of hydrogen which was produced during the copper sulphate experiment may well be attributed to secondary relations between the metal and the salts in solution.

It would appear then that the gases produced by the action of heat upon meteorites are not present as such, but are the products of decomposition of their non-gaseous constituents. It is therefore impossible to draw conclusions as to the former history of a meteorite from the nature of the gases which it gives on heating.

Helium and Argon.

With regard to the state in which helium is present in the minerals from which it is obtained by the action of heat, there is at present no conclusive evidence. It must be present under one of three conditions:—

I. In combination with some constituent of the mineral.
II. Occluded; or in solution in the mineral.
III. Enclosed in cavities under pressure.

Microscopic examination of the minerals, from which

helium has been derived, has failed to reveal the presence of cavities, and, indeed, if we assume that cavities exist, and that they contain all the helium present in the mineral, we have to make further assumptions to explain why the helium escapes when the mineral is heated, although in most cases no disintegration takes place. It seems improbable that the helium is present in the state of solid solution or occlusion, a condition of which we yet know little, for unless we assume that the rate of diffusion of the helium through the mineral in which it is dissolved is infinitely small, the gas should long have escaped into the atmosphere. Further, it is probable that the supposed cases of solution of gases, like hydrogen, in solids such as platinum, palladium, &c., are really cases of chemical combination, as has recently been proved by the researches of Ramsay, Mond, and Shields, and even in meteoric iron it is improbable that the hydrogen is not present as such, but is the product of secondary reactions. Indeed, in the state of our knowledge at present it is impossible to draw a distinction between occlusion and chemical combination.

We are, therefore, forced to the conclusion that helium is present in the minerals in the state of combination with one of its constituents. It may be well to review such positive evidence as exists in favour of such a supposition.

In the first place the gas is not found generally dispersed among crystalline mineral substances, but seems only associated with certain elements, uranium, yttrium, &c., in minerals which are invariably vein products.

It has been pointed out by Professor Ramsay and the author (*Roy. Soc. Proc.*, vol. lxii., p. 325), that in certain cases the evolution of helium from the mineral is accompanied by a considerable evolution of heat, and in one case by a considerable decrease in density. This matter has been dealt with fully in the paper (*loc. cit.*), and is considered as evidence in favour of chemical combination. Julius Thomson (*Zeit. Phys. Chem.*, vol. xxv., p. 112), has confirmed this observation.

A series of experiments were undertaken to determine the conditions under which the minerals gave off helium. It was found that from cleveite helium was evolved, but very slowly, at the temperature of boiling quinoline, and somewhat faster at the temperature of boiling sulphur. At a bright red heat a considerable quantity of helium was obtained, but in no case did the mineral lose the whole of its helium under the influence of heat alone.

By heating cleveite to redness for some hours a mixture of helium, hydrogen, carbon dioxide, and carbon monoxide was obtained; the gas came off readily at first, and appeared finally to cease altogether.

A quantity of the same sample was completely decomposed by means of sulphuric acid (30 per cent) in an exhausted sealed tube. The results are given below:—

	By heating the mineral.	By action of sulphuric acid.
He ..	1·487 c.c. per grm.	3·201 per cent per grm.
H_2 ..	0·367 „	0·333 „
CO_2 ..	2·298 „	

It will be noticed that only half the helium is given off on heating the mineral; this makes it appear probable that if the helium is present in the mineral originally in a state of binary combination the decomposition takes place according to the equation:—

$$XHe_2 = XHe + He.$$

A specimen of fergusonite was also examined, but the results were not altogether satisfactory, as it was found to be practically impossible to completely decompose the mineral by the action of 30 per cent sulphuric acid; strong sulphuric acid appeared to be still more inactive. When fused with acid potassium sulphate a larger yield of helium was obtained, but the mineral was not completely decomposed. The following figures indicate that about half the helium contained in the mineral is liberated under the influence of heat:—

	By action of heat on mineral. C.c. per grm.	By 30 per cent sulphuric acid. C.c. per grm.	Fusion with acid sulphate. C.c. per grm.
He	1·041	1·434	1·813
H_2	0·231	0·163	
CO, &c. ..	0·326		

It is somewhat significant that both cleveite and fergusonite yield hydrogen when decomposed by sulphuric acid. If the helium were present in combination with a metal it would eventually be liberated as a hydride. It is probable that the hydride would be a very unstable compound and would decompose at the moment of formation.

Part of the hydrogen would probably be taken up by the ferric and uranic compounds, and part would escape in the gaseous state. A similar reaction would take place between sulphuric acid, and an iodide, in the presence of a reducible substance, at a higher temperature.

Conclusions.

It would appear that the only evidence on which the assumption that gases of a permanent character, such as hydrogen, carbon monoxide, nitrogen, helium, and argon, exist in the free state in the mineral substances from which they are evolved on heating, rests on certain observations with regard to the cavities which can sometimes be detected by microscopic examination.

The cavities may be either apparently empty or they may contain liquid, and when the mineral is warmed the liquid disappears at a temperature which is a few degrees below the critical point of carbon dioxide or of some hydrocarbon. The fact that the critical temperature of the liquid is a little below the point corresponding to carbon dioxide, in the case of a mineral containing that substance is not, however, of very great significance as pointing to the presence of a permanent gas. A small quantity of methane would produce the same result (Kuenen, *Phil. Mag.*, 1897).

Further, although it can be shown that *compact* minerals do enclose carbon dioxide and hydrocarbons, gases which can easily be liquefied, the analogy cannot be extended to gases such as hydrogen and helium in connection with minerals like chlorite, mica, and cleveite, which exhibit many cleavages.

On the other hand, there is, as I have endeavoured to show, a considerable amount of evidence in favour of the theory which I have put forward:—That in the *majority of cases* where a mineral substance evolves gas under the influence of heat, the gas is the product of the decomposition or interaction of its *non-gaseous* constituents at the moment of the experiment. The results of such experiments cannot, therefore, serve as basis for speculation as the origin and history of the substances in question.

ON THE PREPARATION OF THE SILICIDES OF TUNGSTEN, MOLYBDENUM, CHROMIUM, AND MANGANESE.

By H. N. WARREN, Principal, Liverpool Research Laboratory.

In order to prepare the above-named compounds a quantity of graphitoidal silicon was obtained by fusing together, at a white heat, a mixture consisting of two parts of mineral cryolite and one of sodium silicate; when perfectly liquid, an ingot of aluminium 2 lbs. in weight was introduced into the mass, in order to set free the silicon. Reduction by this means always proceeds tranquilly, although attended with considerable rise in temperature, and in this respect differs greatly to when potassium silicofluoride is employed, the reaction in the latter instance often amounting to explosive violence, and resulting in a serious accident some four years previous, when operating upon a cwt. of melted silicofluoride at the Research Laboratory.

After fusion the silicon, if properly reduced, is found in the form of a perfectly spherical ingot, containing about 10 per cent free aluminium; this is separated by digestion in hot HCl, pure graphitoidal silicon remaining, which after drying should be finely pulverised. Manganese silicide is readily produced by reducing any of the oxides of manganese, in contact with an excess of silicon at a full white heat, the regulus thus procured presenting itself in the form of a well-melted ingot, and possessing a full white metallic lustre. It is very brittle, and readily scratches glass, being soluble with difficulty in ordinary acids, but readily attacked by means of hydrofluoric; it contains on an average from 30 to 40 per cent of silicon.

The chromium compound much resembles the manganese product, but is less readily attacked by reagents and somewhat less fusible, but at the same time possessing greater hardness.

For the preparation of the tungsten and molybdenum silicides a somewhat higher temperature is required, and the author recommends with confidence, in order to carry out the smelting operation, a small oxyhydrogen blast-furnace. An intimate mixture with either oxide of tungsten or molybdenum is next procured, and the furnace urged to its maximum heat, for about twenty minutes, the mixture being lodged in a specially prepared crucible. If the operation has been satisfactorily conducted a well-melted ingot is obtained, containing upwards of 20 per cent silicon, while in other cases, if the heat has been deficient, a metallic half-fused mass, containing various percentages of silicon, is the result. As regards their physical properties, the silicides of either tungsten or molybdenum appear to be highly crystalline and possessed of extreme hardness, some specimens even scratching rock crystals,—comparatively speaking, the tungsten compound ranking as the hardest.

All are with difficulty acted upon by acids, except hydrofluoric acid, whilst at a red heat chlorine attacks all of them readily. No electrical furnaces are required.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending November 30th, 1898.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, December 10th, 1898.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined by us during the month, one was found to be "slightly turbid"; the remainder were all clear, bright, and well filtered.

The rainfall at Oxford during November has again shown a deficiency; the actual fall was 1·86 inches. The average fall for the past thirty years is 2·42 inches; this leaves a deficiency of 0·56 inch, and makes the total deficiency for the year 6·67 inches, or 28·2 per cent.

Our bacteriological examinations of 256 samples have given the results recorded in the following table; we have also examined 44 other samples, from special wells, standpipes, &c., making a total of 300 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	862
New River, filtered (mean of 26 samples) ..	80
Thames, unfiltered (mean of 26 samples) ..	7425
Thames water, from the clear water wells of five Thames-derived supplies (mean of 126 samples)	49
Ditto ditto .. .. highest	435
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	944
River Lea, from the East London Company's clear water well (mean of 26 samples) . ..	11

The bacteriological results for the month have been satisfactory. The East London water supply has been exceptionally good, the average of 26 samples being only 11 microbes per c.c., whereas the mean of 126 samples from the Thames-supplied Companies is 49 per c.c. Both these results prove highly efficient filtration; but it must be confessed that a reduction of the number of microbes to anything as low as 10 or 11 is highly exceptional, and more than could have been expected a few years ago, when between 100 and 200 microbes per c.c. were considered allowable in a potable water.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

A SCHEME FOR THE RAPID ANALYSIS OF BOILER WATERS FOR SCALE-FORMING INGREDIENTS.

By THOS. B. STILLMAN, M.Sc., Ph.D.

The complete analysis of a boiler water presents no difficulties to the analytical chemist, but the time required for the various separations and determinations of the constituents therein often precludes many examinations. Where the chemical analysis is desired for the amounts of the scale-forming ingredients only, a method should be used that is relatively rapid and approximately correct. A scheme embodying such a method whereby the amounts of calcium carbonate, calcium sulphate, magnesium carbonate, and iron oxide could be rapidly determined would be of great service in technical laboratories. In many railroad laboratories the following process is used to determine *total* scale-forming ingredients.

One-half litre of the boiler water is evaporated to dryness in a weighed platinum dish, and the amount of residue determined.

This residue is treated with a solution of alcohol 50 parts, and water 50 parts, and then filtered.

The undissolved matter is designated a scale-forming material.

This method gives, of course, the *total* matter that is scale-forming, but does not indicate the proportions of each constituent.

It is essential to know, in many cases, whether the scale will be calcium sulphate or calcium carbonate or magnesium carbonate.

SCHEME FOR RAPID ANALYSIS OF BOILER WATERS.

(Communicated to the writer by Prof. WM. MAIN, Chemical Expert to New York Filter Co.).

Total solids. Mineral matter. Organic matter. The desired amount of water is evaporated to dryness in a platinum dish and weighed; this residue (1) represents total solids. Ignite, then moisten slightly with distilled water, place in an atmosphere of carbonic acid for half an hour, dry and weigh; this residue (2) is the total mineral matter combined with carbonic acid, as it previously existed, before ignition. The difference in weight between Residue 1 and Residue 2 is the organic matter.

Scale-forming ingredients. Extract soluble matter from Residue 2 with successive small portions of distilled water, in all 50 c.c. or less. Filter through ashless filter; dry the residue adhering to platinum dish. Dry and ignite filter and return the matter it may have retained to the platinum dish, and weigh. The weight of this residue (3) represents the total scale-forming ingredients of the water.

Non-scale-forming ingredients. The filtrate contains the alkalis and magnesia combined with sulphuric acid and chlorine. These may be determined if desired, but are not necessary in this operation. Their aggregate weight may be determined by subtracting Residue 3 from Residue 2.

Treat Residue 3 with hot HCl and filter. Wash well.

Residue. Insoluble mineral matter. Dry, ignite, and weigh as such. SiO_2, &c.

Filtrate.—Add ammonic hydrate in slight excess, boil, and filter.

Residue. $Al_2O_3.Fe_2O_3$. Dry, ignite, and weigh as such.

Filtrate.—Add solution of ammonic oxalate in slight excess, set aside ½ hour. Wash with water containing ⅛ its volume of ammonic hydrate.

Residue. Dry, ignite, and weigh as CaO.

Filtrate.—Add solution of sodic phosphate with constant stirring. Set aside ½ hour; filter, wash with water containing ⅛ its volume of ammonic hydrate.

Residue. Dry, ignite, and weigh as $Mg_2P_2O_7$ and calculate to MgO.

Filtrate.—Acidify with HCl, add solution of $BaCl_2$ in slight excess, boil, set aside ½ hour, filter, wash well with hot water.

Residue.—$BaSO_4$. Dry, ignite, and weigh as $BaSO_4$, and calculate to SO_3. This amount of SO_3 is combined with CaO to form $CaSO_4$ that exists in Residue 3.

SiO_2, &c. $Al_2O_3.Fe_2O_3$. CaO. MgO. SO_3.

The scale formed by calcium sulphate is hard, compact, and exceedingly difficult of removal, whereas the scale formed by calcium and magnesium carbonates is more or less porous and not difficult of removal.

A scheme of analysis, that has been used by the author, and showing many advantages for correct determinations with rapidity, is appended.

The remaining CaO, as well as the MgO, are calculated to carbonates and the amounts of $CaSO_4$, $CaCO_3$, $MgCO_3.SiO_2$, &c., and $Al_2O_3.Fe_2O_3$ should equal the weight of Residue 3. Professor Main states regarding the above scheme as follows:—

"Careful tests made with artificial mixtures of sulphate of lime and carbonate of lime show that the error due to solubility of calcium sulphate in water is hardly weighable, especially after it is converted into anhydrous sulphate by heat.

"The amount of sulphate of lime which will fail to precipitate from solution, and that which can be dissolved (in any reasonable time) from the solid state with pure water alone, are very different things. This supposed solubility has previously prevented chemists from using methods similar to the above scheme for a rapid method of boiler water analysis."—*The Stevens Indicator*, October, 1898.

Science Gossip.—After a successful career of over thirty years, *Science Gossip*, the favourite journal for amateurs devoted to natural, physical, and applied science, has just entered upon independent offices, at 110, Strand. This magazine has latterly been greatly improved, and the articles deal with subjects of most recent discovery or theory. The editorial management is still under the control of Mr. John T. Carrington, assisted by Miss F. Winstone. There are also several specialists as departmental editors for such sections as physics, microscopy, astronomy, botany, geology, zoology, meteorology, &c.

THE ACTION OF NITRIC ACID ON TIN IN THE PRESENCE OF THE METALS OF THE IRON GROUP.

By F. H. VAN LEENT.

WHILE testing for lead in tin plate I had occasion to observe the reaction mentioned by Rose on the subject of the separation of tin from other metals by means of nitric acid. The tin coating of the sheet iron was scraped off with a hard steel knife, in such a manner that, besides the metal to be analysed, a relatively large proportion of iron was also detached. This mixture was treated with nitric acid of specific gravity 1·2, and at the end of the reaction the liquid was evaporated to dryness on the water bath. The residue moistened with water was completely dissolved. Rose points this out as a very interesting circumstance ("Analytische Chemie," ii., 284). It is, in fact, an exception to the rule, according to which we should expect to obtain the tin in the state of oxide and retain the iron in solution. To avoid this inconvenience in an analysis of bronzes containing iron and tin, Fresenius advises precipitating the tin with sulphuric acid or nitrate of ammonium in the solution of metallic chlorides obtained by successive treatments with nitric and hydrochloric acids ("Quantitative Analysis," i., 264, 265). With the object of discovering what compound of tin could have been formed, I treated mixtures of powdered iron and tin, either finely granulated or in small clippings, with nitric acid. I then evaporated to dryness and took up the residue with water. The formation of a nitrate of tin was hardly probable in view of the great instability of this compound, which is easily decomposed by heating. To obtain great solubility it is necessary, during the evaporation, to take care to mix the ferric nitrate, which adheres to the sides of the porcelain dish, with the stannic oxide which is found at the bottom.

In these experiments I have found that the minimum

quantity of iron which will hold a convenient quantity of tin in solution is about one-fifth or one-sixth of the latter. Small quantities of iron, 0·03 grm. to 1 grm. of tin for example, dissolves only a small quantity of the other metal. With 0·05 grm. of iron a part of the stannic oxide is rendered soluble, and the viscous residue is very difficult to collect on the filter. The dry material attracts water when exposed to air, and becomes soft and sticky; moistened with water, it first becomes soft, and then dissolves fairly rapidly. We can also treat the iron and the tin with nitric acid separately, and then unite the products of the reaction. After evaporation to dryness we find that the stannic oxide, insoluble at first, has passed to the soluble state.

Twice its own volume of concentrated nitric acid is added to the solution. A slightly yellow precipitate is then formed: this is left to settle, and washed two or three times by decantation with nitric acid of 1·2 sp. gr. It is then collected on a hard filter-paper. The mother-liquor does not contain any tin, the compound being completely insoluble in fairly concentrated nitric acid. It is useless to try to eliminate all the iron, either by several washings or by repeated precipitations of the re-dissolved material, since it obstinately retains a quantity of iron which it is difficult to diminish, even with large quantities of solvent. The precipitate is dried in an exsiccator over quicklime, or caustic potash *in vacuo*.

After desiccation it appears in the form of hard resinous lumps; moistened with water, they become disintegrated and decrepitate very slightly; the mass then softens, and eventually dissolves slowly, giving a viscous solution. With only a little water we can obtain a gelatinous product resembling silicic acid. If kept in the exsiccator its solubility gradually diminishes, so that old preparations give up very little tin to the water. The solution contains tin in the form of metastannic acid, as is shown by the following experiments. For the purpose of observing the action of different reagents, it is better to dissolve a portion of the undried precipitate. Nitric acid in excess, dilute sulphuric acid, and oxalic acid; the two latter—even in small quantities—give a precipitate with the solution.

The same result is obtained by boiling the liquid. It is worthy of remark that the primitive solution, which contained a relatively large quantity of iron, is not precipitated by boiling. Further, we can evaporate this solution to dryness without the stannic compound becoming insoluble, while the purified product leaves a soluble residue by desiccation on the water-bath.

Sulphuretted hydrogen precipitates a deep brownish green sulphide from a solution acidulated with a little hydrochloric acid. The sulphide is only deposited slowly. Bichromate of potassium gives a yellow precipitate resembling chromate of lead.

Caustic soda gives a white precipitate very slightly soluble in an excess of the reagent.

Stannous chloride in a slightly acid solution gives a yellow precipitate.

Hydrochloric acid added in excess separates metastannic acid, which is re-dissolved on boiling. In this boiled solution sulphuretted hydrogen precipitates ordinary yellow stannic sulphide. The metastannic chloride has thus passed to the ordinary state.

By avoiding an excess of hydrochloric acid we prevent the separation of the metastannic acid. This solution, kept in the cold, gives a white amorphous precipitate, which is deposited very slowly, on the addition of chloride of cæsium or rubidium.

According to Behrens the two modifications of stannic acid are distinguished in this manner ("Analyse Qualitative Microchimique," p. 63).

As I was not able to obtain soluble metastannic acid in a state of purity, I analysed it such as it was after precipitation with nitric acid. As it persistently retains iron and nitric acid I performed these experiments considering them from the point of view indicated by Van Bemmelen in his researches on the so-called "hydrogels" (*Rev. d. Trav. Chim. des Pays Bas.*, 1888, pp. 91 and 101—103; *Landwirtschaftliche Versuchsstationen*, 1888, p. 90). The metastannic acid was dried in an exsiccator *in vacuo*, over caustic potash or quicklime, and analysed after having been kept under these conditions for varying lengths of time. I estimated the loss of weight by calcination, the amounts of ferric and stannic oxides, and the nitric acid. The separation of the iron and the tin in the calcined residue was effected by heating it with a mixture of soda and sulphur.

By dissolving the melted mass in water we obtain a green liquid, caused by the solubility of the sulphide of iron as shown by Rose (*loc. cit.*, p. 284). On digesting, after having added chloride of ammonia all the iron is deposited. However, the sulphide is not quite pure—it still contains some sulphide of tin; it is therefore necessary to re-dissolve it in dilute hydrochloric acid. Sulphuretted hydrogen is passed through the solution, and the sulphide of tin removed, and the excess of sulphuretted hydrogen driven off by boiling. The iron is then transformed to the ferric state by peroxide of hydrogen, and precipitated by ammonia. The calcined residue represents the ferric oxide. For the estimation of the tin, in some samples, I preferred to treat the green solution with hydrochloric acid, then saturate with sulphuretted hydrogen, and carefully calcine the sulphide of tin, adding a little carbonate of ammonium, to obtain stannic oxide. The filtrate serves for the estimation of the iron. The nitric acid was estimated by Schlœsing's method.

Analyses.

A. The metastannic acid precipitated by nitric acid and washed once with dilute nitric acid by decantation, was dried *in vacuo* over quicklime for five days (*a*), and for fifteen days (*b*).

Matter taken.	Loss by calcination.
a. 0·6562 grm.	0·1448 grm. = 22·1 per cent.
b. 0·5620 „	0·0938 „ = 16·7 „

Matter taken.	Nitric oxide.	Nitric acid (N_2O_5).
a. 1·2528 grms.	57·4 c.c. of NO at 18·5° and 760 m.m.	= 10·2 per cent.
b. 1·4776 „	60·6 c.c. of NO at 18·5° and 760 m.m.	= 9·1 „

B. The metastannic acid was divided into two parts, which were dried over caustic potash in as perfect a vacuum as possible. The material was in a thin layer.

a. Analysis after five days:—

Matter taken.	Loss by calcination.	Ferric oxide.
0·6576 grm.	0·1414 grm. = 21·5 p. c.	0·0474 = 7·2 p. c.

Calculated for the calcined matter, 9·2 p. c.

	Nitric oxide.	Nitric acid (N_2O_5).
1·8730 grms.	70·7 c.c. of NO at 16° and 767 m.m.	7·8 per cent.

After twenty-two days:—

Matter taken.	Nitric oxide.	Nitric acid (N_2O_5).
0·8684 grm.	29·8 c.c. of NO at 15° and 769 m.m.	7·8 per cent.

b. Second part after twenty-nine days:—

1·8184 grms. 64·2 c.c. of NO at 14° and 760 m.m. 8 p.c.

C. Prepared like A. Analyses after ten, and twenty-five days *in vacuo*:—

Matter taken.	Loss by calcination.	Ferric oxide.
a. 0·5456 grm.	0·1094 grm. = 20·1 p.c.	0·0396 grm. = = 7·3 p.c.
b. 0·7742 „	0·1342 „ = 17·3 „	0·0574 grm. = = 7·4 p.c.

Calculated for the calcined matter, 9·1 and 9 per cent.

To observe the influence of heat on the loss of nitric acid, a sample was kept in a place where the temperature

often rose to 35°. The desiccation then took place very rapidly.

a. Analysis after nine days:—

Matter taken.	Nitric oxide.	Nitric acid (N_2O_5).
0·8598 grm.	28·4 c.c. of NO at 13° and 770 m.m.	7·6 per cent.

b. After twenty-two days:—

0·7626 grm.	24 c.c. of NO at 11·5° and 759 m.m.	7·2 ,,

In a portion prepared this summer and kept *in vacuo* several weeks, the proportion of nitric acid went even as low as 4·6 per cent N_2O_5. The loss of weight by calcination was then found to be 20·3 per cent. The material had an opaque appearance, and was hardly soluble at all. Analysis shows that in the exsiccator the material constantly loses water and nitric acid, and also that there is no constant relationship between the ferric oxide and the nitric acid. We may therefore conclude that ferric nitrate, if it exists in the precipitate, is a very unstable compound which is decomposed under these conditions. The proportion of iron is nearly constant after washing with nitric acid, and it is difficult to further diminish it. These results are in accordance with those of M. Van Bremmelen on the "hydrogels" of stannic oxide, which have a composition variable according to the vapour tension of the water, and obstinately retain other substances. In order even to partly dissolve these substances it is necessary to use large quantities of the solvent.

Samples which have been kept a long time in the exsiccator, and have thus lost their water and nitric acid, become very difficulty soluble. The solution of an apparently dry metastannic acid has a strongly acid reaction. By neutralising the solution as accurately as possible with decinormal soda, with phenolphthalein as indicator, all the metastannic acid is precipitated. The result of a volumetric analysis is also well in accord with the estimation of the nitric acid: 1·7760 grm. of the dry precipitate = 37·3 c.c. of 1/10 N soda = 11·3 per cent of N_2O_5. Schloesing's method gives 9·7 per cent.

The neutral point need not be determined very exactly, the colouration of the phenolphthalein disappears slowly on account of the presence of metastannic acid, which already has an acid reaction. The metastannic acid is re-dissolved by adding a slight excess of nitric acid. It seems thus, that this modification of stannic acid requires a certain amount of nitric acid or of ferric nitrate to retain its solubility.

I have also examined how some of the metallic nitrates of the iron group behave with regard to stannic oxide; nitrates of chromium, aluminium, nickel, cobalt, and manganese for example. For 1 grm. of tin I use 3 grms. of crystallised nitrate of chromium or aluminium, and 1 grm. of the nitrates of the other metals. The salts having been added to the tin the whole was treated with nitric acid, and carefully evaporated to dryness. The result found was that the nitrates of chromium and aluminium exercised the same action as ferric nitrate, and that the stannic oxide became soluble. The nitrates of the other metals left it intact. To sum up I must conclude that stannic oxide is rendered soluble only by the nitrates derived from the oxides M_2O_3, while this property does not belong to those of the form MO; also that stannic oxide is then present as a soluble modification of metastannic acid belonging to the class of bodies called "hydrogels."—*Moniteur Scientifique*, December, 1898.

A New Iodide of Tungsten.—Ed. Defacqz.—The author has prepared a new iodide of tungsten, the tetriodide WI_4, by the action of liquid hydriodic acid of tungsten hexachloride. This substance is black and crystalline, slowly changing when in contact with air. It has a density of 5·2 at 18°; it is decomposed slowly by cold water, rapidly by boiling water, giving in both cases the brown oxide and hydriodic acid.—*C. R.*, cxxvii., No. 15.

THE

PREPARATION OF ZIRCONIUM NITRIDES.*

By J. MERRITT MATTHEWS.

THE ammonia derivative of titanium tetrachloride, $TiCl_4{\cdot}4NH_3$, when heated in a current of ammonia gas, yields a nitride of titanium (Rose, *Pogg. Ann.*, xvi., 57; Persoz, *Ann. Chim. Phys.*, xliv., 321). This nitride has been given the formula Ti_3N_4, and has been thoroughly investigated. From this knowledge it was of interest to ascertain if a zirconium nitride could be prepared from its ammonia derivative. The attempt was made, and a corresponding zirconium nitride was obtained.

A portion of the zirconium tetrachloride derivative with ammonia, $ZrCl_4{\cdot}8NH_3$, obtained by passing dry ammonia gas into an ethereal solution of the zirconium salt (*J. Am. Chem. Soc.*, xx., 821), was placed in a porcelain boat and gradually heated to redness in a current of nitrogen in a glass combustion tube. Abundant fumes of ammonium chloride were given off and condensed in the cooler part of the tube; the residue left in the boat was pearl-grey in colour, and in the form of a light powder. On heating this residue in a current of hydrogen, ammonia was evolved, which was conducted into a standardised solution of hydrochloric acid, and thus determined. When this compound was heated in the air it lost weight, and became pure white in colour, passing over into the dioxide, ZrO_2, and the zirconium was estimated in this form.

Analyses.

I. 0·2416 grm. material gave:—
0·0836 grm. ammonia = 0·0688 grm. nitrogen = 28·47 per cent nitrogen.
0·0654 grm. material gave:—
0·0629 grm. zirconium dioxide = 0·0465 grm. zirconium = 71·10 per cent zirconium.

II. 0·2006 grm. material gave:—
0·0691 grm. ammonia = 0·0569 grm. nitrogen = 28·36 per cent nitrogen.
0·2572 grm. material gave:—
0·2469 grm. zirconium dioxide = 0·1827 grm. zirconium = 71·05 per cent zirconium.

These analyses show a close approximation to the formula Zr_3N_8.

	Calculated for Zr_3N_8.	Found. I.	Found. II.
Zirconium	70·82	71·10	71·04
Nitrogen	29·18	28·47	28·36

The residue left after heating this nitride in a current of hydrogen was lead-grey in colour and amorphous; it was soluble in hydrofluoric acid, but proved to be insoluble in the other mineral acids. This appearance and behaviour leave little doubt but that this residue consists of metallic zirconium, the action of hydrogen being to reduce the nitride to the metal with the formation of ammonia.

In the preparation of the pure nitride care must be exercised in excluding all air from the apparatus, otherwise a mixture of the oxide and nitride will be obtained. In the preparation of the sample used for the above analyses, all the air was first driven out by means of a vigorous current of carbon dioxide gas, after which a current of nitrogen was allowed to pass through the apparatus for two hours before the compound was heated.

Zr_2N_3.—This second nitride was prepared by a procedure differing somewhat from that used in the first. Zirconium tetrachloride was placed in a porcelain boat and gradually heated to redness in a current of dry ammonia gas. By this method the ammonia derivative,

* Contribution from the John Harrison Laboratory of Chemistry, From the *Journal of the American Chemical Society*, xx., No. 11, November, 1898.

$ZrCl_4 \cdot 4NH_3$, was at first formed (*J. Am. Chem. Soc.*, xx., 823). This by the action of the heat was broken down into a nitride of zirconium, together with the formation of ammonium chloride, which was given off in dense fumes and condensed in the cooler part of the tube, leaving the nitride in the boat in the form of a grey amorphous powder. It was somewhat darker in colour than the preceding compound, but resembled it exactly in its behaviour. The nitrogen was estimated by heating the compound in a current of hydrogen, and collecting the ammonia evolved in a standardised solution of hydrochloric acid. By heating another portion in the air it became pure white in colour, increasing in weight, leaving the dioxide, ZrO_2, from the weight of which the zirconium was estimated.

Analyses.

I. 0·2537 grm. material gave :—
0·0478 grm. ammonia = 0·0402 grm. nitrogen = 19·23 per cent nitrogen.

0·2462 grm. material gave :—
0·2707 grm. zirconium dioxide = 0·2001 grm. zirconium = 81·27 per cent zirconium.

II. 0·2217 grm. material gave :—
0·0523 grm. ammonia = 0·0431 grm. nitrogen = 19·42 per cent nitrogen.

0·2546 grm. material gave :—
0·2792 grm. zirconium dioxide = 0·2064 grm. zirconium = 81·05 per cent zirconium.

	Calculated for Zr_2N_3.	Found. I.	II.
Zirconium	81·18	81·27	81·05
Nitrogen	18·82	19·23	19·42

Mallet (*Jsb. Chem.*, clxxxv., 145) obtained a nitride of zirconium by heating the metal in ammonia gas; it is described as a dark grey amorphous powder. A similar product, and one identical in every way with that obtained in this present research, was also prepared by Mallet by heating anhydrous zirconium tetrachloride in ammonia gas. This procedure is exactly similar to that described above; but Mallet made no investigation into the constitution of the compound which he prepared in this manner.

A nitride of thorium has been prepared by Chydenius (*Jsb. Chem.*, 1863, 194) by a procedure identical with that used in the preparation of the first zirconium nitride above described. This nitride of thorium is spoken of as a white amorphous powder, and behaves in a manner very similar to the zirconium compound. Thus the analogy existing between these two elements is once more strikingly manifested.

ON THE SEPARATION OF NICKEL AND COBALT BY HYDROCHLORIC ACID.*

By FRANKE STUART HAVENS.

A QUANTITATIVE separation of nickel and cobalt by a process analogous to that published from this laboratory for the separation of aluminum and iron (Gooch and Havens, *Am. Journ. Sci.*, vol., iv., ii., 416), has been put forward in a recent paper by E. Pinerùa (*Gaz. Chim. Ital.*, vol. xxvii., 56). The process may be described briefly as follows:—The hydrous chlorides of nickel and cobalt (0·3—0·4 grm.) are dissolved in a little water, and to the solution are added 10 to 12 c.m.³ of aqueous hydrochloric acid, and 10 c.m.³ of ether, and the whole, contained in a little beaker surrounded with water and ice, is saturated with gaseous hydrochloric acid. The cobalt, which remains in solution, is decanted off and the yellow insoluble nickel chloride washed with a previously prepared solution of ether saturated with hydrochloric acid gas at a low temperature. The nickel is determined by known methods, preferably as the sulphate. The author claims very precise results for the process, but gives no experimental proof of his work. Previous to the appearance of this paper my experiments upon the solubility of nickel chloride in an ether-hydrochloric acid solution, such as used in our process for the separation of aluminum and iron, which is practically the same in proportions as that used by Pinerùa to effect precipitation, had shown that, while nickel chloride is somewhat insoluble in such a mixture, the degree of insolubility is not sufficient for a quantitative separation. Since the appearance of Pinerùa's work I have been over the ground again, and have reached the same conclusions as before, as shown in the following experiments.

When a solution of 0·2 grm. of nickel chloride (free from iron and cobalt) in 7 c.m.³ of aqueous hydrochloric acid was saturated with hydrochloric acid gas at a temperature of −2° C. (obtained by immersing the container in a mixture of ice and salt) no precipitation resulted. When, however, an equal volume of ether was added and the whole was again saturated with hydrochloric acid gas a yellow precipitate formed, while the supernatant liquid still remained of a deep green colour. The solution was filtered quickly through asbestos in a filter crucible, and the clear filtrate after evaporation with sulphuric acid was electrolysed. The metallic deposit of 0·0020 grm. proved to be pure nickel; for when dissolved in nitric acid it gave no test for iron with potassium sulphocyanide or ferrocyanide, and neither the apple-green hydroxide nor the black sulphide, prepared by the usual methods, showed any trace of cobalt in the borax bead. It is obvious, therefore, that nickel chloride is not fully precipitated under these conditions and that the green colour of the solution is due to nickel in solution and not to traces of iron, as Pinerùa has supposed (*loc. cit.*) A second experiment similar to the first showed a solubility of the nickel chloride represented by 0·0018 grm. of metallic nickel. It is evident, then, that the solubility of nickel chloride in this mixture of aqueous hydrochloric acid and ether thoroughly saturated with hydrochloric acid gas is not far from an amount represented by 0·0020 grm. of metallic nickel for every 14 c.m.³ of solution.

Still another experiment, in which nickel chloride representing 0·0020 grm. of metallic nickel was treated with 14 c.m.³ of the ether-hydrochloric acid solution and the whole saturated for one hour at a low temperature with hydrochloric acid gas without precipitation, showed the same thing.

When the nickel chloride remaining on the asbestos was washed with about 40 c.m.³ of a mixture of equal parts ether and aqueous hydrochloric acid saturated with hydrochloric acid gas, the washings evaporated with sulphuric acid and treated by the battery gave a deposit of metallic nickel weighing 0·0027 grm.—an amount proportionately less than that found in the filtrate proper.

Although employing a mixture of aqueous hydrochloric acid and ether saturated with gaseous hydrochloric acid for the precipitation, Pinerùa has advised the use of pure ether saturated with gaseous hydrochloric acid for the washing. In my experiments with such a mixture I find that in it the hydrous nickel chloride is practically insoluble and that 30 c.m.³ of the washings of the precipitated chloride with such a mixture gave no deposit of nickel by the battery. It seemed possible, therefore, that by reducing the water present to the lowest possible amount necessary to dissolve the chlorides to be treated the precipitation of the nickel might be made more complete. The experiments of the following table were made to put this idea to the test.

Solutions of the pure chlorides of nickel and cobalt, carefully purified and freed from other metals and each other, were, after conversion to the form of the sulphate, standardised by the battery. Weighed portions of these solutions were taken in a small beaker, evaporated to dry-

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, 1898, vol. vi., p. 396.

ness, the dry salts dissolved in as little water as possible (about 1 c.m.^{3}), 10 to 15 c.m.^{3} of ether added, and the whole saturated with hydrochloric-acid gas, the beaker being meanwhile immersed in running water and cooled to about 15° C. When saturation was complete the precipitated chloride was caught on asbestos in a filter crucible, washed thoroughly with a previously saturated solution of ether, dissolved in water, evaporated with sulphuric acid and determined as metallic nickel by the battery. The cobalt in the filtrate was recovered by evaporation and electrolysis in like manner.

Experiments 1, 2 and 3 of the accompanying table show that by this process the nickel is thrown down quantitatively, and experiments 2 and 3 show that in the presence of a few milligrms. of the cobalt salt the separation of a small amount of nickel is sharp. The residue of nickel in these experiments gave no test for cobalt with the borax bead. When, however, the cobalt is present to the amount of a few centigrms. as in 4, 5, and 6, the precipitated nickel chloride, which forms a hard mass, includes the cobalt salt, so that even a large quantity of washing solution (100 c.m.^{3} was used in experiment 6) cannot remove it.

	Nickel taken as the hydrous chloride.	Nickel found.	Error.	Cobalt taken as the hydrous chloride.	Cobalt found.	Error.
1.	0·0068	0·0066	−0·0002	—	—	—
2.	0·0090	0·0090	0·0000	0·0030	—	—
3.	0·0090	0·0091	+0·0001	0·0123	0·0127	+0·0004
4.	0·0469	0·0490	+0·0021	0·0700	—	—
5.	0·0468	0·0503	+0·0035	0·0700	—	—
6.	0·0472	0·0493	+0·0021	0·0700	—	—

From the experiments described it is obvious that the process as proposed by Pinerùa will not give a complete precipitation of the nickel chloride. Nickel chloride is, however, practically insoluble in pure ether saturated with hydrochloric acid gas and can be separated from small quantities of the soluble cobalt salt in that medium. In the presence of even a few centigrms. of the cobalt chloride, however, the process is not practicable on account of the inclusion of the cobalt by the massive nickel chloride. It is possible that by repeated solutions and re-precipitations the nickel salt might be sufficiently freed from the cobalt, but the process must naturally be long and tedious.

In closing the author wishes to express his gratitude to Professor Gooch for kind suggestions.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 1st, 1898.

Professor Dewar, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Samuel William Allworthy, The Manor House, Antrim Road, Belfast; John Frank Blackstraw, Holly Bank, Marton, Chelford, Cheshire; Henry Cort Harold Carpenter, 109, Banbury Road, Oxford; Frank Cope, 30, Leeds Road, Dewsbury; Thomas James Cozens, The Grammar School, Middleton-in-Teesdale, Co. Durham; Samuel Godfrey Hall, 19, Aberdeen Park, Highbury, N.; Thomas Anderson Henry, 37, Chelsea Gardens, S.W.; Thomas Luxton, 4, Cavendish Square, Margaret Street, Hull; James Roberts, jun., 43, Great Western Road, Glasgow; Frederick William Skirrow, Graystongill, Bentham, Lancaster; Charles Emerique Szarasy, 19, Weymouth Street, Portland Place, W.; Thomas Wilson Wormell, 184, Burrage Road, Plumstead, S.E.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected.

Hugh Poynter Bell, B.A.; Reginald Arthur Berry; Walter Birkett; Thomas Henry Boardman, B.A.; Marston Taylor Bogert, A.B., Ph.B.; Arthur Brooke, B.A.; Johannes Christian Brünnich; John Paul de Castro; Charles Robert Carroll; David Leonard Chapman, B.A.; William Samuel Crouch; Alfred V. Cunnington, B.A.; W. Brown Davidson, M.A., Ph.D.; Samuel Dickson; Francis Alfred Drake, B.Sc.; James Edward Ferguson; Edward Gardner; John Naish Goldsmith, B.Sc., Ph.D.; E. B. Hadley; Alfred Hartridge, B.A.; John Haworth; Alexander Garden Hendry; George W. F. Holroyd, B.A.; Walter Howe; Thomas Hill-Jones; Benjamin Jordan-Smith; Reginald Arundale Kay; John Charles Mascarenhas; William Lash Miller, B.A., Ph.D.; Thomas Arthur Nightscales; William Pollard, B.A., Ph.D.; John Armstedt Ray, jun., B.A.; Edmund Milton Rich; Gilbert Rigg; Henry John Rofe, B.A.; Henry J. S. Sand, Ph.D.; Richard Seligman; George Senior, B.A.; Samuel Smiles, jun., B.Sc.; Basil Steuart; Ambrose Walton; Frederick Louis Wilder; Charles William Tuthill Woods; John Henry Young, B.Sc.

The following papers were read:—

144. "*The Oxidation of Polyhydric Alcohols in presence of Iron.*" By Henry J. Horstman Fenton, M.A., and Henry Jackson, B.A., B.Sc.

In continuation of the study of the influence of ferrous iron on the oxidation of various hydroxy-compounds, the authors are engaged in investigating the behaviour of various alcohols, and the present communication gives an account of the results which, so far, have been obtained.

The monhydric alcohols (methylic, ethylic, propylic, isopropylic, and amylic), under the conditions employed, give entirely negative results either in presence or absence of iron. But in the case of all the polyhydric alcohols examined (ethylene glycol, glycerol, erythritol, mannitol, dulcitol, and sorbitol), it is found that the presence of ferrous iron exerts a remarkable influence on oxidation by means of hydrogen dioxide. In the absence of iron practically no change is produced, but, in its presence, very considerable rise of temperature occurs in all cases, and the alcohol is vigorously oxidised.

Ethylene glycol yields glycollic aldehyde, but apparently no glyoxal. With glycerol the product appears to be glyceraldehyde with little or no dihydroxyacetone. From erythritol a product yielding erythrosazone is obtained, and mannitol gives mannose. The yields, generally, are remarkably good as compared with those obtained by oxidation with nitric acid, &c., and in this way it is easy to obtain mannose directly from mannitol without first preparing the hydrazone. The authors are attempting to isolate tetrose in a similar way.

As in the case of tartaric acid, it is found that certain of these polyhydric alcohols may be similarly oxidised by atmospheric oxygen in presence of ferrous iron and of sunlight.

145. "*The Occurrence of Hyoscyamine in the Hyoscyamus Muticus of India.*" By Wyndham R. Dunstan and Harold Brown.

The authors find that the stem and leaves of the Indian *Hyoscyamus muticus* contain about 0·1 per cent of hyoscyamine, and that the alkaloid can be extracted in a pure state from this plant more readily than from ordinary henbane. The plant is fairly abundant in the Punjab and Beluchistan, and is likely to prove of value both as a drug and as a source of hyoscyamine.

Discussion.

Professor Dunstan, in reply to Mr. Groves, Mr. David Howard, and Mr. Page, said it was possible that age and climate might have some influence in changing the hyoscyamine and forming other mydriatic alkaloids. There was every reason to believe that the physiological action

of the drug was principally due to the alkaloid it contains, and not to any other constituent.

Dr. W. H. Perkin, F.R.S., then took the chair, and the following paper was read:—

146. "*The Comparative Colour of the Vapour of Iodine in Gases at Atmospheric Pressure and in a Vacuum.*" By James Dewar, LL.D., F.R.S.

Recently, having had occasion to compare iodine with other substances as a means of obtaining vacua in the construction of vessels used for the storage and manipulation of liquid air in low temperature research, some facts about the behaviour of the vapour of iodine have been observed which deserve to be recorded. Pure iodine in the solid state is usually stated to be perfectly opaque to light, but this is not the character of iodine distilled and condensed on a surface of glass at temperatures between −180 and −190 in vacuum test tubes or bulbs by the use of liquid air. Under such conditions it is easy to get transparent films of iodine of varying grades of thickness showing brilliantly the colours of thin plates by reflection, and to keep them permanently as long as the low temperature is maintained. The first addition of liquid air to the vacuum bulb or test tube containing excess of solid iodine causes instant precipitation of an opaque film, but this can be avoided by cooling the iodine, which has been caused to sublime to the lower part of the outer test tube or bulb, by a preliminary treatment with a little solid carbon dioxide.

In this condition, when the inner surface of the vacuum vessel is cooled with liquid air, the iodine can only deposit from an atmosphere of great tenuity, and when a given thickness of deposit is reached, any increase can be stopped by removing the vessel from the liquid carbon dioxide and placing it in liquid air. In the same way films of other substances can be deposited, which may be useful in the examination of many physical problems. Stas says that pure iodine gives no visible vapour at the ordinary temperature, but this is contrary to the author's experience. Samples of iodine, obtained from cuprous iodide, from iodoform, and from solution of iodine in potassium iodide, and in sufficient quantity to ensure saturation, gave, in half-litre flasks, a visible colour to the atmosphere at the ordinary temperature. When, however, a similar flask containing the same iodine was exhausted of air, the colour of the atmosphere was markedly less, and this distinction remained even when the flasks were heated side by side in a water bath. If the iodine vapour diffused into an atmosphere of carbon dioxide, hydrogen, or oxygen, in similar flasks, instead of into air, the colour remained the same; but in all cases it was much more marked than in one from which the gaseous atmosphere, other than iodine, had been in great part removed by the air pump. No change in the mode of filling the air and vacuum flasks made the difference in colour disappear, although a dozen flasks have been filled from time to time. No change in the character of the results was effected by subliming the iodine from anhydrous baryta, and keeping it in flasks for months with excess of the latter, nor was any apparent difference produced when the flasks containing the baryta were repeatedly heated at the boiling point of water. This seems to prove that neither water vapour nor hydrogen iodide has anything to do with the cause of the difference in colour of the iodine vapour in the air and vacuous flasks. It is not necessary to use flasks, as two lengths of glass tubing, an inch or less in diameter and a foot or more in length, when heated side by side in a steam or water bath, show the difference of colour.

To obtain an approximate value of the tension of the saturated vapour of iodine at about the ordinary temperature, a Rankine formula of two terms was calculated, taking the known pressure at 58·1° as 4·9 m.m. and that at 113·8° as 87 m.m. These gave:—

(1) $\log P = 9{\cdot}3635 - 2872/T$ m.m.

If, however, the tension at 85° and 114·1° are selected for calculation,—

(2) $\log P = 10{\cdot}0392\ 3137/T$ m.m.,

where T is the absolute temperature. From formula (1) the tensions in m.m. of mercury at 0° and 11° are respectively 0·07 and 0·18. The weight of iodine in a litre would thus become about 1 and 1·94 m.grms. at 0° and 11° respectively. In order to check this calculation, the quantity of iodine required to saturate a litre of dry air at 0° and 11° was determined by passing a slow current of air over a column of the substance, and subsequently absorbing the iodine from the saturated air by passing it through a caustic potash solution. The alkaline solution, after acidifying, was titrated with sodium thiosulphate. The results of the experiments were as follows:—

	M.grms. per litre.	Pressure in m.m. of mercury.
0°	0·24	0·017
11°	1·25	0·087
30°	4·70	0·358

In each case, the calculated tension is less than that deduced from the first vapour pressure equation. The values approach those given by Arctowski (*Zeit. Anorg. Chem.*, 1896, vol. xii., 427) as a deduction from his experiments on the volatilisation of iodine. From this, it would follow that the second equation for the tension is the better. In the liquid state, the tensions are well represented by (3) $\log P = 7{\cdot}924\ 2316/T$ m.m. From formula (2), the molecular latent heat of solid iodine is 14430 units, and for the liquid condition from (3) the value is 10653. The experimental value of the latent heat of liquid iodine given by Favre is 6000 units. From this, it would follow that the latent heat of volatilisation requires to be re-determined. It is interesting to observe that the number of heat units required to dissociate the molecule of iodine is 28500, or roughly, twice the calculated latent heat of the solid.

The various experiments recorded lead to the conclusion that the phenomenon is a real one, although some factor that has been neglected may explain it; at any rate, it is difficult to avoid getting the result. Assuming it be true, its explanation then remains to be considered. It is well known that the vapour pressure in a vacuum is often greater than in air at atmospheric pressure. On the other hand, Professor J. J. Thomson, in his work entitled "Application of Dynamics to Physics and Chemistry," p. 169, discusses this very question. He shows that the effect of the pressure of an inert gas must be to raise the vapour pressure of a substance diffusing into it above that produced by the diffusion of the same substance into a vacuous space. Taking the equation which he there developed as being applicable to iodine, the difference between the two conditions of pressure should amount to $\frac{1}{440}$ of the whole. Now the question arises whether this amount is sufficient to explain the difference of colour or whether it is necessary to bring in other factors which may operate, such as solution of solids in gases under pressure, dissociation, or want of equilibrium. Further experiments will be required before a definite answer can be given.

Hannay and Hogarth first showed that alcohol vapour above its critical point, and therefore at a pressure above 60 atmospheres, can dissolve solids like potassium bromide or iodide, and Cailletet, a little later, found that liquid carbon dioxide was dissolved by air under high compression. Dr. Villard has recently made a series of experiments on the same subject, in which he proves that bromine and iodine dissolve in air or oxygen under high compression. He says: "L'iode se dissout egalèment en quantité sensible dans l'oxygène, mais le phénomène n'est bien visible qu'a partir de 100 atmosphères et dans des tubes de 5 millimetres de diametre au moins."

The experiment exhibited would appear to show that the pressure of one atmosphere is sufficient to produce a

sensible difference of colour in the case of iodine vapour diffused in air and in a vacuum. For the present, it may be regarded as a lecture illustration of the rapidity of volatilising iodine in an air space as contrasted with a vacuous one.

Discussion.

Dr. Thorpe thought that the phenomenon which the President had brought to the notice of the meeting was highly interesting and suggestive. It seemed to him, after watching the experiment shown to them during its whole course, that the character of the colour of the resulting vapours was so markedly different as to lead to the inference that something more than a mere dilution of colour due to an actual difference in the amount of vapour present had occurred. He could not help comparing the phenomenon with the well-known difference in colour of various solutions of iodine in alcohol, carbon disulphide, chloroform, &c., and thinking that molecular dissociation was taking place. Perhaps in this connection it might be worth while to make a comparative spectroscopic study of the vapours in the two conditions.

Professor F. D. Brown said that he, too, had remarked the much browner colour of the iodine vapour in the vacuous tube. Remembering the fact that iodine in brown solutions is in a different molecular condition from that in violet solutions, it seemed probable that the vapours in the two tubes were also in different molecular conditions.

With regard to the suggestion that the iodine was in some way dissolved in the gas, he stated that one of his students in New Zealand had ascertained that equal volumes of different gases at the same temperature and pressure took up exactly equal quantities of iodine, whereas it was probable that if iodine dissolved in a gas as a solid dissolves in a liquid differences in solubility would have been found.

Mr. Elworthy, in reference to the solubility of solids in gases at temperatures above their critical points, and under pressure, said that when in Bombay he gave instructions for some vulcanised rubber to be placed in a vessel with carbon dioxide at about 5 or 6 atmospheres pressure; instead of this about 5 pounds of the gas were introduced into a vessel usually employed to contain 15 pounds of liquefied carbon dioxide. At temperatures below the critical point a certain amount of liquefied gas would have been present, but as the temperature was between 87° and 90° F., the gas was in the condition of a vapour under pressure. On opening the vessel and allowing the gas to escape, it was found that practically all the sulphur had been dissolved out of the rubber, the surface of which was covered with a thin crust of sulphur crystals.

Mr. L. M. Jones asked whether any attempt had been made to determine the actual concentration of the iodine in the two cases; and also whether the apparent solubility of a solid in gas at high pressure might not be actually due to the increase of vapour pressure predicted by Professor J. J. Thomson.

Dr. Travers pointed out that the critical phenomena observed when the air confined over liquid carbon dioxide was compressed at constant temperature could not be produced by conditions similar to those which were present in the case of the iodine and air. When air was compressed in contact with any liquid, it dissolved and produced a mixture of constantly decreasing critical temperature. Consequently, supposing that sufficient air were present, it should in any case be possible by exerting sufficient pressure to produce a mixture whose critical temperature was the temperature of the experiment. The phenomenon could have nothing to do with the solution of the solid or liquid in the gas.

Dr. Forster inquired whether iodine had been imprisoned in atmospheres other than a mixture of nitrogen and oxygen. If, as was suggested, the phenomenon in question is a case of solution, differences in appearance similar to that subsisting between solutions of iodine in alcohol and in carbon disulphide, might be expected in tubes containing iodine enclosed with various inert gases.

The President, in reply, said that the spectroscope had not been used in his experiments, and bearing in mind the character of the absorption spectrum of iodine, he anticipated it would be difficult to obtain any information as to the character of the phenomenon by its employment. The possibility of dissociation had not escaped attention, having been mentioned in the paper. All that he could say was that at present he could not specifically state that the difference in the behaviour of iodine under the two conditions was due to one or other of the possible causes to which he had referred. Iodine enclosed in tubes containing gases such as carbon dioxide, nitrogen, hydrogen, and oxygen gave appearances indistinguishable from those observed in similar tubes containing air.

CORRESPONDENCE.

SIMPLE APPARATUS FOR THE ESTIMATION OF CARBON DIOXIDE.

To the Editor of the Chemical News.

Sir,—In the Chemical News for December 16 (vol. lxxviii., p. 293), Mr. W. H. Barker describes and figures a "Simple Apparatus for the Estimation of Carbon Dioxide."

May I be allowed to remark—

1. That this apparatus only differs from the well-known apparatus of Bunsen by the shape of the flask; and,

2. That this modification has already been described by me in my "Traité de Chimie Analytique Minerale, Qualitative and Quantitative," vol. ii., p. 991, with a second modification, which consists in replacing the bulb tube for the acid with a small test-tube; the manipulation with this seems to be more convenient. See the accompanying figure extracted from my book.—I am, &c.,

Dr. L. L. de Koninck.

NOTICES OF BOOKS.

Some Interesting Soil Problems. By Milton Whitney. Reprint from *Year-book of Department of Agriculture for* 1897.

It is found in the United States that, as a rule, soil problems in the extreme West are simpler and easier to study than anywhere else in the country; the soils themselves are more uniform in their texture, and there is less variation from the normal climatic conditions. When rainfall is scanty, as in this district, the rocks are more apt to disintegrate with comparatively little decomposition; this disintegration has in most cases reached to a considerable depth, so that there is seldom a difference between the soil and the subsoil, as there is in the moister climate of the East.

Some of these soils absorb water so readily, and lose it by evaporation so slowly, and yet supply the plants so regularly and abundantly, that they can stand long periods

of drought without the crops suffering to any noticeable extent.

In the great wheat areas in the northern part of California, and other adjacent places, the soils produce fine crops of wheat without irrigation; they are strictly summer crops, and the soils have the power of retaining the winter rains and giving up the moisture when it is needed, and, as the rainfall is but from 13 to 18 inches per annum, it is considered very doubtful, or wholly improbable, that any of the water leaks away and runs off in the country drainage. If this power of retaining water can be imparted to other soils, and especially to those of the East, it will be of very great value and importance to the farmer.

The first question to solve is the distribution of the rainfall and the average depth of wells,—that is, the depth to standing water; another question which can be determined experimentally is, What is the minimum quantity of water required by these soils to enable them to support a crop? It is not sufficient that a soil should be very retentive of moisture, but it should also conserve it, losing very little by evaporation, but at the same time the water must move rapidly up to the roots of the plant; it is thus not only the water capacity of the soil, but also its ability to supply this water to the plants, that determine its agricultural value.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxvii., No. 15, October 10, 1898.

Preparation and Properties of Calcium Nitride.—Henri Moissan.—If a piece of crystalline calcium is suspended in an atmosphere of pure dry nitrogen, and the temperature gradually raised, the metal slowly begins to absorb the gas, and its white colour changes to yellow. As the temperature increases, the colour deepens. At a red heat the combination takes place with incandescence; the calcium burning in the nitrogen gas, and the absorption taking place very rapidly. The best method of preparing calcium nitride is to place the crystalline calcium in a nickel boat; the boat being placed in a tube of the same metal. A current of pure dry nitrogen is then passed through the apparatus. The nitride thus formed is in the form of little transparent brownish yellow crystals having a density of 2·63 at 17°. It corresponds to the formula N_2Ca_3; it unites easily with chlorine, bromine, iodine, oxygen, sulphur, and phosphorus, and is decomposed by carbon at a high temperature. With anhydrous alcohol it gives ammonia and calcium ethylate; and it decomposes cold water, giving ammonia.

Crystalline Tungsten Dioxide and Tungsto-Lithium Tungstate.—L. A. Hallopeau.—Crystalline dioxide of tungsten can be prepared from paratungstate of lithium; the latter, unlike the paratungstates of potassium and sodium, being capable of complete reduction by hydrogen at a red heat. The dioxide obtained is a brown powder composed of very small crystals belonging to the regular system, and having a formula WO_2. In order to obtain from paratungstate of lithium a tungsten bronze, the lithium salt must be reduced by an agent other than hydrogen. It has already been found that blue quadrilateral plates are formed by the action of tin on lithium tungstate. The author has repeated this preparation, and made an accurate analysis of the product formed. The analysis confirms the formula $Li_2W_5O_{15}$, which can be written $Li_2O.WO_3+WO_2.3WO_3$.

Thermometric Study of the Suboxide and the Peroxide of Sodium.—M. de Forcrand.—The author has found the heat evolved when the three oxides of sodium Na_3O, Na_2O_2, and Na_2O are decomposed by water. (1) The difficulty in the case of the suboxide Na_3O is owing to the violence of the reaction; the determination must be done in the absence of air, to prevent the cooled hydrogen from inflaming. The mean of two experiments gives 97·78 calories as the heat evolved during this reaction. (2) The dioxide can be dissolved directly in the water of the calorimeter; the chief difficulty being that the oxygen is not all evolved, but is partially absorbed to make peroxide of hydrogen; it is better therefore to dissolve the dioxide in dilute hydrochloric acid; 119·79 calories is the number found. (3) 19·39 calories is the number for the decomposition of the protoxide Na_2O.

On the Combinations of Lithium Chloride with Methylamine. — H. Bonnefoi. — Pure anhydrous lithium chloride absorbs methylamine gas (as it does ammonia), forming with it three successive combinations, of which the dissociation and heat of formation have been studied by the author. To render the salt porous and voluminous, dry ammonia gas is passed over it, and subsequently completely expelled by heat in a current of dry nitrogen. During absorption, the chloride swells up, and remains in this condition, which is the most favourable for the absorption of methylamine. The combination $LiCl+CH_3NH_2$ is formed above +65°. $LiCl+2CH_3NH_2$ is produced between +40° and +65°, and $LiCl+3CH_3NH_2$ below 40°. The heats of solution in water of methylamine gas and of these three substances having been determined, the following equations are deduced:—

1. $LiCl(sol.)+CH_3NH_2(gas)=$
$=LiCl+CH_3NH_2(sol.)+13{\cdot}82$ cal.
2. $LiCl(sol.)+2CH_3NH_2(gas)=$
$=LiCl+2CH_3NH_2(sol.)+25{\cdot}88$ cal.
3. $LiCl(sol.)+3CH_3NH_2(gas)=$
$=LiCl+3CH_3NH_2(sol.)=36{\cdot}69$ cal.

It follows from this research that the formula of Clapeyron is perfectly applicable to the dissociation of these compounds.

A Di-iodine Derivative of Quinoline.—C. Istrati.—So far no general method has existed for introducing halogen atoms into ring compounds containing nitrogen, such as pyridine and quinoline. The author describes a method by which these iodine derivatives may be easily prepared. Taking the case of quinoline:—Quinoline sulphate, dissolved in excess of sulphuric acid, is treated with iodine for several days; the degree of substitution which occurs depending on the quantity of iodine introduced and the temperature to which the mixture is subjected. On pouring the product into much water, a brownish deposit is obtained, and, finally, a small quantity of a white deposit. The precipitate is treated with potash and then extracted with alcohol. Crystals of a new substance, the di-iodine derivative of quinoline, are obtained. Analysis gives it the formula $C_9NH_5I_2$. There are also found—in a portion less soluble in alcohol, but soluble in chloroform—derivatives containing more than two atoms of iodine in the molecule. The white second precipitate crystallises from alcohol and corresponds to the formula C_9NH_6I. The production of these substances is also accompanied by a sulphonated derivative of quinoline.

Phenyl- and Phenylene-phosphoric Acids.—P. Genvresse.—The author gives a description of the preparation and properties of phenyl-phosphoric acid,—

$$C_6H_5.PO_4H_2;$$

phenylene-diphosphoric acid,—

$$C_6H_4\begin{matrix}PO_4H_2(1)\\PO_4H_2(4)\end{matrix};$$

and oxyphenylphosphoric acid,—

$$C_6H_4\begin{matrix}PO_4H_2(1)\\OH(2)\end{matrix};$$

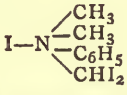
These are crystalline substances obtained by the action of phosphoric anhydride upon phenol and polyatomic phenols, respectively.

Volumetric Estimation of Ethyl Aldehyd.— X Rocques.—This paper describes the volumetric estimation of ethyl aldehyd in dilute alcoholic solution (*e.g.*, as it occurs in brandies). The method depends on the reaction between acid sulphites and aldehyds. This reaction, in the case of solutions containing only 1 per cent of aldehyd, is not complete in the cold for several hours. A normal solution of sodium acid sulphite is made, and a known volume added to the alcoholic solution of aldehyd. After standing, this is titrated with normal iodine solution, and hence the percentage of aldehyd calculated.

Thermic Constants of Isoamylmalonic Acid.— G. Massol.—The heats of solution in water of this acid and its neutral potassium salt are given; also the heat of neutralisation of the acid by potash, and the results compared with the numbers obtained for its isomer, suberic acid.

Bulletin des Travaux de la Société de Pharmacie de Bordeaux, July, 1898.

Compounds obtained with Iodoform and the Tertiary Aromatic Amines.—G. Denigés.—The author was led to undertake these experiments when attempting to generalise Caro's reaction by which fuchsine was obtained by heating large quantities of iodoform with aniline. He found that the secondary and tertiary amines behaved in the same manner as the primary ones, and often gave better results, especially in the case of dimethylaniline. The action of heat on iodoform is always the cause of the liberation of iodine, and it was thought probable that the production of these coloured derivatives might be preceded by the dislocation of the iodoformic molecule, with the fixation on the amines of the products of this splitting up. Such products, both definite and stable, were obtained with the tertiary amines. Under the influence of sunlight the dissolved iodoform is decomposed into free iodine and an iodised residue, which at once combine with the amine, giving an iodo-substituted quaternary iodide of ammonium.



Analogous compounds have been obtained with di-iodoform.

The Use of Binoxide of Lead in Analysis; Application to Urines and Fermented Liquors.—A. Loubiou.—The author has applied the oxidising properties of binoxide of lead, the intensity of which can be varied according to the neutrality or acidity of the surrounding medium, or its absorbent properties for simplifying and bringing into practical form the estimation of certain principles of urine and fermented liquors. The method of detecting and estimating albumen in urine is to add one drop of phenolphthalein to 10 c.c. of the sample, then add drop by drop normal soda until the colour is slightly pink, add to the liquid 1 to 1·5 grms. of binoxide of lead, shake well for a minute, and filter; a few drops of Tanret's reagent is added to the solution, which then takes its original colour. On boiling, if albumen is present, a cloudiness or a precipitate is formed according to the quantity present. The author is convinced by the results obtained, that binoxide of lead does not attack the albumenoid matter in a neutral solution, while it allows of the complete clarification of the liquid; several comparative results are given to prove this.

September, 1898.

The Use of Binoxide of Lead in Analysis; Application to Urines and Fermented Liquors.—H. Loubiou.—For the estimation of the reducing matters of cider, place 10 c.c. of cider in a 100 c.c. flask with sufficient normal soda to neutralise it, add 0·2 c.c. of acetic acid and make up to 100 c.c., shake well, then pour the whole into a 150 c.c. flask, and add 2 grms. of binoxide of lead; cork up and shake well for a minute, then filter; in the flask used for the reduction place 25 c.c. of Bonnan's solution and bring up to boiling point, then pour in four or five drops of the filtered liquid and boil again; repeat this until a yellow colour appears, then add only two drops at a time; this must be continued until a blackish red colour appears, which indicates the end of the reaction. Let n be the number of cubic centimetres of the filtrate used and T the titration value of the Bonnan's solution; 1 c.c. of filtrate corresponds to T/n and 1000 c.c. to $T/n \times 1000$, but the cider was first diluted to 1 in 10, so its real value in glucose will be $T/n \times 1000 \times 10$. In a large number of experiments most satisfactory results have been obtained by this method. The same method is applied to beer and urines with equal success.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Artificial Manures.—Can any reader tell me the name and price of the three best books on the manufacture of artificial manures; what are the percentages of potassium chloride, potassium sulphate, salt, and iodine in (1) dry sea-weed, and (2) in kelp? Also the name and address of any firm or private person in Germany or London who could supply me with tubes of the nitrifying organisms of the soil?—J. H.

MEETINGS FOR THE WEEK.

Tuesday, Jan. 3rd, Thursday, 5th, Saturday, 7th.—Royal Institution, 3. (Christmas Lectures). "On Astronomy," by Sir Robert Stawell Ball, F.R.S., &c.

Wednesday, 4th.—Society of Arts, 7. (Juvenile Lecture). "Hands and Feet," by Prof. F. Jeffrey Bell.

THE GRAHAM MEDAL, to be awarded for Original Research in any branch of Chemical Science, is now open to competition. Information regarding the conditions under which the award will be made can be had on application to the Secretary of the Philosophical Society of Glasgow, 207, Bath St., Glasgow.

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